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$Er_2O_3-SiO_2$ SYSTEMS

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In previous communications [1-4] the phase diagrams of the binary systems of silica with yttrium, lanthanum, and gadolinium were published. The $Dy_2O_3-SiO_2$ and $Er_2O_3-SiO_2$ systems were studied by the method described in the cited communications. Specimens were prepared from dysprosium oxide containing a total of less than 0.6% of other rare earth oxides, erbium oxide (99.11%) containing a total of 0.85% of other rare earth elements, and powdered rock crystal (99.90% SiO_2).

Dysprosium oxide, fired at 1000°, has a cubic structure and refractive index $\underline{n}=1.88$; its melting point is 2210°. Dysprosium oxide crumbles into a powder after fusion in an electric arc, even when very rapidly cooled. Evidently, out of the melt there crystallizes a noncubic phase, which, owing to the high rate of polymorphic transformation, cannot stabilize and, changing into the cubic phase, causes the specimen to disintegrate. However, the specimen, after fusion in the arc, contains a certain amount of a high-melting phase, as can be seen from comparison of x-ray diffraction curves of dysprosium oxide fired at 1000° and dysprosium oxide fused in an arc (Fig. 1), and also by comparing the two differently treated oxides under a microscope. The average refractive index of the high-melting phase is $\underline{n}=1.975$.

Curtis and Johnson [5], from an x-ray study of rare earth element oxides fired at low temperature, and also after annealing at 1400°, reported that they detected only one cubic phase for Dy_2O_3 and oxides of rare earth elements of higher atomic numbers. Our experiments cause us to place dysprosium oxide also in the group of rare earth element
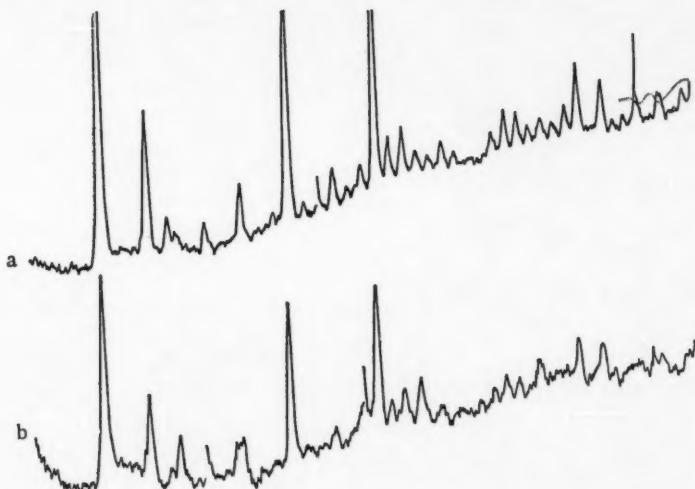
Fig. 1. X-ray diffraction curves of dysprosium oxide. A) Fired at 1000°; B) fused in an arc.

TABLE 1. Results of Annealing Experiments for the $Dy_2O_3-SiO_2$ System

Composition (wt. %)		Temp. (°C)	Duration	Phase*
Dy_2O_3	SiO_2			
95	5	2100	20 sec	Glass
		2000	30 »	Dy_2O_3 + glass
92,5	7,5	1850	30 »	Glass
		1800	30 »	Dy_2O_3 + glass
		1750	1 min	Dy_2O_3 + 1:1
90	10	1900	30 sec	Glass
		1800	45 »	1:1 + glass
86,13	13,87	1950	20 »	Glass
		1900	30 »	1:1
83,5	16,5	1700	60 min	1:1 + 2:3
80,6	19,4	1950	20 sec	Glass
		1900	20 »	2:3
		1850	30 »	2:3
		1700	30 min	2:3
		1600	9 hr	1:1 + 1:2
77	23	1900	20 sec	Glass
		1850	20 »	2:3 + glass
		1750	1 min	2:3 + glass
		1700	5 »	1:2 + 2:3
75,6	24,4	1850	20 sec	Glass
		1800	25 »	2:3 + glass
		1750	30 »	2:3 + glass
		1730	10 min	2:3 + 1:2 + glass
		1700	30 »	1:2
		1750	30 sec	Glass
		1700	1 min	1:2 + glass
70	30	1700	2 min	Glass
		1650	15 »	1:2 + glass
67,42	32,58	1700	2 »	Glass
		1650	5 »	1:2 + glass
		1600	30 »	1:2 + cristobalite
		1550	30 »	1:2 + cristobalite
65	35	1700	5 »	Glass
		1650	10 »	Glass
		1600	7 »	1:2 + cristobalite
		1550	10	1:2 + cristobalite
60	40	1900	30 sec	Glass
		1800	1 min 30 sec	Two glasses
		1700	2 min	Two glasses
		1650	3 hr	Cristobalite + glass
		1600	7 »	Cristobalite + 1:2
50	50	2100	25 sec	Glass
		2050	15 »	Two glasses
		1950	15 »	Two glasses
		1700	11 min	Two glasses
		1650	3 hr	Two glasses
40	60	2300	20 sec	Cristobalite + glass
		2200	15 »	Glass
		1900	45 »	Two glasses
30	70	2350	15 »	Two glasses
		2300	15 »	Two glasses
		1900	15 »	Glass
20	80	2300	20 »	Two glasses
		2100	30 »	Two glasses
5	95	200	30 »	Glass
		1900	1 min	Two glasses
				Glass
				Two glasses

* $1:1-Dy_2O_3 \cdot SiO_2$; $2:3-2Dy_2O_3 \cdot 3SiO_2$; $1:2-Dy_2O_3 \cdot 2SiO_2$.

TABLE 2. Results of Annealing Experiments for the Er_2O_3–SiO_2 System

Composition (wt. %)		Temp. (°C)	Duration	Phase*
Er_2O_3	SiO_2			
92,7	7,3	2000	20 sec	Er_2O_3 + glass
90	10	1950	20 »	Glass
		1900	20 »	Er_2O_3 + glass
		1850	30 »	Er_2O_3 + 1:1 + (eutectic)
86,40	13,6	2000	20 »	Glass
		1950	20 »	1:1 + glass
80,9	19,1	1950	20 »	Glass
		1900	20 »	2:3 + glass
78	22	1800	30 »	Glass
		1780	1 min	2:3
76,1	23,9	1850	30 sec	Glass
		1800	30 »	1:2 + glass
72,5	27,5	1800	30 »	Glass
		1750	30 »	1:2 + glass
		1650	30 »	1:2 + SiO_2
70	30	1750	30 »	Glass
		1700	10 min	1:2 + glass
		1600	5 hr	1:2 + SiO_2
68	32	1750	1 min	Glass
		1670	5 »	SiO_2 + 1:2
65	35	1800	1 »	Glass
		1650	30 »	SiO_2 + 1:2
60	40	2000	20 sec	Glass
		1900	20 »	Two glasses
		1750	20 »	Two glasses
		1650	15 min	SiO_2 + 1:2
50	50	2200	15 sec	Glass
		2100	15 »	Two glasses
60	40	2200	15 »	Two glasses
70	30	2300	30 »	Glass
		2200	30 »	Two glasses
		1750	15 min	Two glasses
90	10	2000	30 sec	Two glasses
95	5	2000	30 »	Glass
		1800	1 min	Two glasses (very little of one)

* 1 : 1—$Er_2O_3 \cdot SiO_2$; 2 : 3—$2Er_2O_3 \cdot 3SiO_2$; 1 : 2—$Er_2O_3 \cdot 2SiO_2$.

TABLE 3. Optical Properties and Densities of Dysprosium and Erbium Silicates

Name and formula of compound	Refractive indicies			Bire-fring-ence	Opti-cal sign	Optical axes	Density (g/cm²)
	n_g	n_m	n_p				
Oxyorthosilicate						Biaxial, optic axial angle ~88°	
$Dy_2O[SiO_4]$	1,865		1,847	0,018			
$Er_2O[SiO]_4$	1,825		1,807	0,018			6,80
Orthosilicate							
$Dy_4[SiO_4]_3$		1,853	1,838	0,015	(—)	Uniaxial	
$Er_4[SiO_4]_3$		1,800	1,780	0,020			6,22
Pyrosilicate							
$Dy_2[Si_2O_7]$	1,765		1,757	0,008	(+)	Biaxial	
$Er_2[Si_2O_7]$	1,768		1,740	0,028			6,10

TABLE 4. X-Ray Examination of Compounds of the $Dy_2O_3-SiO_2$ and $Er_2O_3-SiO_2$ System

Dy₂O₃·SiO₂		Er₂O₃·SiO₂		2Dy₂O₃·3SiO₂		2Er₂O₃·3SiO₂		Dy₂O₃·2SiO₂		Er₂O₃·2SiO₂	
d/n	I/I₀	d/n	I/I₀	d/n	I/I₀	d/n	I/I₀	d/n	I/I₀	d/n	I/I₀
4,09	24	4,08	12	4,04	37	4,62	28	4,09	36	4,63	17
3,88	22	3,91	46	3,57	12	3,88	26	3,44	66	4,47	17
3,40	15	3,56	41	3,23	42	3,53	16	3,24	39	3,36	28
3,14	46	3,37	12	3,07	49	3,36	14	3,10	34	3,22	62
3,08	50	3,15	54	2,88	30	3,22	100	2,89	82	3,13	16
2,81	100	3,03	82	2,79	72	3,16	34	2,724	77	3,02	44
2,75	65	2,93	100	2,74	70	3,02	96	2,627	37	2,94	14
2,72	51	2,675	30	2,70	56	2,93	64	2,528	32	2,699	100
2,038	33	2,555	68	2,48	47	2,72	78	2,466	60	2,490	22
1,933	51	2,428	43	2,443	81	2,687	88	2,294	100	2,439	14
1,876	33	2,275	36	2,410	28	2,546	29	2,083	70	2,260	36
1,821	67	2,190	93	2,312	53	2,491	28	1,973	12	2,168	41
1,796	38	2,037	29	2,223	100	2,428	33	1,855	37	2,129	23
1,769	46	2,009	34	2,189	51	2,267	62	1,830	48	2,055	7
1,742	57	1,989	30	2,150	37	2,176	78	1,753	37	1,908	21
1,692	33	1,941	21	2,087	28	2,13	30	1,694	41	1,842	16
1,526	24	1,853	39	1,926	21	2,047	17	1,654	50	1,788	53
1,484	28	1,820	54	1,874	14	1,913	26	1,629	34	1,768	31
1,464	33	1,749	52	1,855	19	1,847	26	1,580	39	1,728	32
1,438	36	1,729	55	1,819	42	1,815	29	1,542	45	1,690	30
1,419	24	1,683	48	1,790	23	1,787	47	1,477	41	1,676	38
1,302	17	1,641	14	1,767	26	1,775	39	1,457	52	1,645	22
1,276	17	1,620	21	1,740	21	1,726	64	1,396	30	1,581	47
1,253	14	1,572	59	1,683	28	1,689	47	1,257	41	1,541	17
1,239	31	1,516	79	1,654	28	1,645	22	1,223	14	1,487	16
1,222	29	1,467	29	1,618	23	1,579	66	1,162	27	1,419	15
1,214	33	1,452	48	1,533	42	1,512	40			1,394	30
		1,404	23	1,480	30	1,449	22			1,350	6
		1,375	11	1,446	51	1,388	33			1,335	7
		1,333	21	1,427	30	1,266	16			1,293	7
		1,295	14	1,383	28	1,221	29			1,252	13
		1,269	34	1,345	19	1,145	21			1,222	26
		1,220	30	1,256	16	1,083	26			1,181	7
		1,203	23	1,210	19					1,131	15
		1,190	20	1,162	23					1,115	13
		1,178	12	1,14	16					1,106	10
		1,167	11							1,083	23
		1,135	29							1,058	13
		1,124	25								
		1,063	18								
		1,023	14								
		1,014	14								

oxides possessing polymorphism, which agrees with recent data obtained by Shafer and Roy [6]. Erbium oxide differs from dysprosium oxide in that it does not disintegrate after heating in an arc. The optical properties and x-ray diffraction curves of Er_2O_3 fired at 1000° and fused in an arc are similar. Evidently, erbium oxide exists only in cubic form in the temperature range from 1000° to its melting point; its refractive index is $\underline{n} = 1.95$, and its melting point is 2290°.

The phase diagram of the $Dy_2O_3-SiO_2$ system, constructed from the results of firing and annealing experiments, given in Table 1, is shown in Fig. 2. The existence of three compounds, of composition $Dy_2O_3 \cdot SiO_2$, $2Dy_2O_3 \cdot 3SiO_2$, and $Dy_2O_3 \cdot 2SiO_2$ in the system was established. Compounds of analogous composition were also obtained for the $Er_2O_3-SiO_2$ system, the phase diagram of which is shown in Fig. 3, and the results of the firing and annealing experiments for this system are given in Table 2. The optical properties and densities of the obtained compounds are given in Table 3, and the calculated interplanar distances are given in Table 4.

The oxyorthosilicates $Dy_2O[SiO_4]$ and $Er_2O[SiO_4]$ melt without decomposition. The orthosilicates $Dy_4[SiO_4]_3$ and $Er_4[SiO_4]_3$ also melt without decomposition, but they are stable only in a specific temperature range, below which they decompose into orthosilicates and pyrosilicates. Such behavior was established on the basis of the following ex-
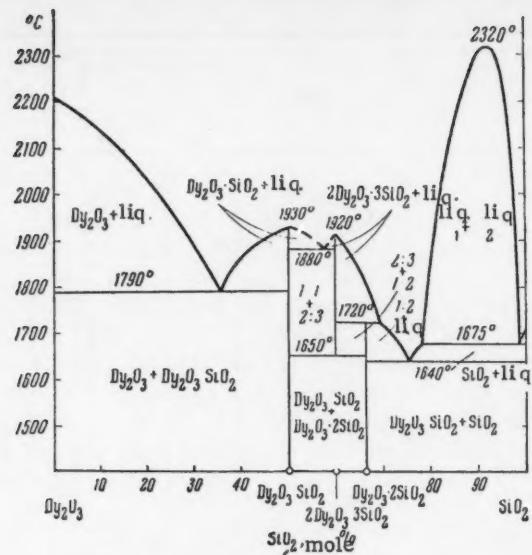
Fig. 2. Phase diagram of the $Dy_2O_3 - SiO_2$ system (in mole percent).
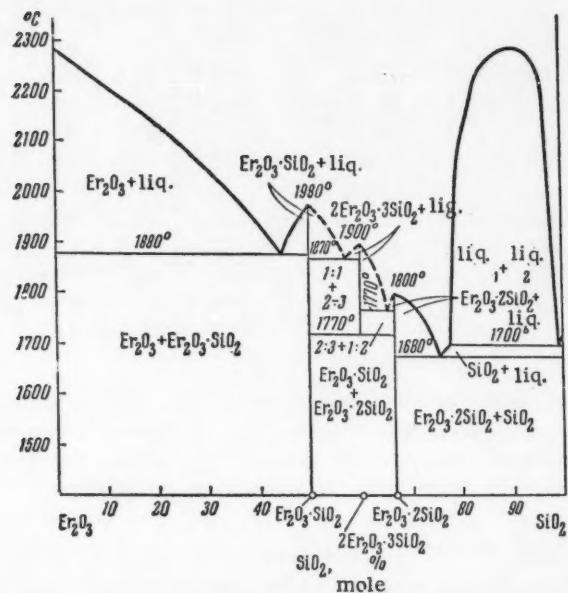
Fig. 3. Phase diagram of the $Er_2O_3 - SiO_2$ system (in mole percent).

TABLE 5. Invariant Points of the $Dy_2O_3-SiO_2$ System

Phases	Process	Composition				Temp. (°C)
		wt. %		mole %		
		Dy_2O_3	SiO_2	Dy_2O_3	SiO_2	
Dy_2O_3 + $Dy_2O_3 \cdot SiO_2$ + liquid	Eutectic	92	8	64.9	35.1	1790
$Dy_2O_3 \cdot SiO_2$ + liquid	Fusion	86.13	13.87	50	50	1930
$Dy_2O_3 \cdot SiO_2$ + $2Dy_2O_3 \cdot 3SiO_2$ + liquid	Eutectic	82	18	42	58	1880
$2Dy_2O_3 \cdot 3SiO_2$ + liquid	Fusion	80.6	19.4	40	60	1920
$Dy_2O_3 \cdot SiO_2$ + $Dy_2O_3 \cdot 2SiO_2$ + $2Dy_2O_3 \cdot 3SiO_2$	Reaction in the solid state	80.6	19.4	40	60	1650
$2Dy_2O_3 \cdot 3SiO_2$ + $Dy_2O_3 \cdot 2SiO_2$ + liquid	Incongruent fusion	73	27	30.4	69.6	1720
$Dy_2O_3 \cdot 2SiO_2$ + α-cristobalite + liquid	Eutectic	67	33	24.50	75.50	1640
α-Cristobalite + liquid A + liquid B		63	37	21.50	78.50	1675
α-Cristobalite + liquid A + liquid B		2	98	0.33	99.67	1675

TABLE 6. Invariant Points of the $Er_2O_3-SiO_2$ System

Phases	Process	Composition				Temp. (°C)
		wt. %		mole %		
		Er_2O_3	SiO_2	Er_2O_3	SiO_2	
Er_2O_3 + $Er_2O_3 \cdot SiO_2$ + liquid	Eutectic	89	11	56	44	1880
$Er_2O_3 \cdot SiO_2$ + liquid	Fusion	86.5	13.5	50	50	1980
$Er_2O_3 \cdot SiO_2$ + $2Er_2O_3 \cdot 3SiO_2$ + liquid	Eutectic	83	17	43.5	56.5	1870
$2Er_2O_3 \cdot 3SiO_2$ + liquid	Fusion	81	19	40	60	1900
$Er_2O_3 \cdot SiO_2$ + $Er_2O_3 \cdot 2SiO_2$ + $2Er_2O_3 \cdot 3SiO_2$	Reaction in the solid state	81	19	40	60	1720
$2Er_2O_3 \cdot 3SiO_2$ + $Er_2O_3 \cdot 2SiO_2$ + liquid	Eutectic	77	23	34.5	65.5	1770
$Er_2O_3 \cdot 2SiO_2$ + liquid	Fusion	76.1	23.9	33.4	66.6	1800
$Er_2O_3 \cdot 2SiO_2$ + SiO_2 + liquid	Eutectic	67	33	24.2	75.8	1680
α-Cristobalite + liquid A + liquid B		65	35	22.6	77.4	1700
α-Cristobalite + liquid A + liquid B		3	97	0.5	99.5	1700

periments. Mixtures of the oxides, conforming to the orthosilicate composition (oxide ratio 2 : 3), after complete fusion in an arc or microfurnace crystallized in the orthosilicate phase. The same mixture of oxides, annealed for 5-10 hours at 1600-1650°, gave two other compounds—oxyortho— and pyrosilicates. On the other hand, orthosilicates obtained by crystallization from the melt and subsequently annealed at 1600° for four hours contained together with the orthosilicate, its decomposition products—the two other compounds. In all these experiments the phase compositions were established by x-ray and microscopic analysis.

Dysprosium pyrosilicate, $Dy_2[Si_2O_7]$, melts with decomposition into the orthosilicate $Dy_4[SiO_4]_3$ and liquid. Primary resorbed orthosilicate crystals and secondary elongated dysprosium pyrosilicate crystals can be seen in the microphotograph (Fig. 4). We first detected a sharp change in the properties of the rare earth silicates during a study of erbium pyrosilicate, $Er_2[Si_2O_7]$. All the pyrosilicates of rare earth elements with atomic number lower than that of erbium (Y, La, Sm, Gd, and Dy) melt with decomposition into orthosilicate and liquid. In contrast to these, erbium pyrosilicate melts without decomposition, and there is a corresponding maximum on the phase diagram of the $Er_2O_3-SiO_2$ system. $Er_2[Si_2O_7]$ also differs from the other pyrosilicates by having considerably higher birefringence. These differences in the properties of the silicates are evidently connected with change in the electronic structures and dimensions of the rare earth element ions.

The compositions and temperatures of the oxyortho- and orthosilicate eutectics in both systems, and also the ortho- and pyrosilicate eutectic on the $Er_2O_3 - SiO_2$ phase diagram, are shown by broken lines since we failed to establish the appropriate values with sufficient accuracy. The products obtained by firing and annealing mixtures, the compositions of which lie between those of the mentioned silicates, were shown, from x-ray and microscopic data, to comprise two specific phases. The path of the liquidus curve, in this region, was established by means of a series of observations during concurrent fusion of two specimens in a microfurnace. The compositions of such "pairs" of specimens differed by 1-2 %.

Separation of the melt occurs in both systems. The upper critical point of the separation region, in the system containing dysprosium, occurs at a temperature of 2320° and composition 28% Dy_2O_3, 72% SiO_2. The corresponding values for the $Er_2O_3 - SiO_2$ system are 30% Er_2O_3, 70% SiO_2, and the critical point temperature is 2280°. The compositions and temperatures of the invariant points of the $Dy_2O_3 - SiO_2$ and $Er_2O_3 - SiO_2$ systems are given in Tables 5 and 6 respectively.

Fig. 4. Primary resorbed crystals of $2Dy_2O_3 \cdot 3SiO_2$ and secondary crystals of $Dy_2O_3 \cdot 2SiO_2$.

SUMMARY

1. The phase diagrams of the binary systems $Dy_2O_3 - SiO_2$ and $Er_2O_3 - SiO_2$ were studied and constructed.

2. Compounds of the types oxyorthosilicates ($Dy_2O[SiO_4]$ and $Er_2O[SiO_4]$), orthosilicates ($Dy_4[SiO_4]_3$ and $Er_4[SiO_4]_3$), and pyrosilicates ($Dy_2[Si_2O_7]$ and $Er_2[Si_2O_7]$) were synthesized. The properties of these compounds were studied.

3. The compound $Er_2[Si_2O_7]$, in contrast to other pyrosilicates of rare earth elements with atomic number lower than that of erbium, melts without decomposition and has higher birefringence.

4. The limits of the separation regions in the studied systems were established, and their upper critical points were determined.

5. Dysprosium oxide polymorphism was detected. Erbium oxide is not polymorphic.

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SILICATES OF THE RARE EARTH ELEMENTS

COMMUNICATION 6. PHASE DIAGRAMS OF THE BINARY SYSTEMS $Sm_2O_3-SiO_2$ AND $Yb_2O_3-SiO_2$, AND COMPARISON OF THESE SILICATES WITH THE OTHER RARE EARTH ELEMENT SILICATES WHICH HAVE BEEN STUDIED

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As we have already pointed out in previous communications [1-6], recently rare earth elements and their compounds have become important materials for use in new techniques (nuclear, rocketry, semiconductor); they find a still wider use in different branches of the national economy. A series of investigations have shown that rare earth elements can be used as luminophore activators, and in some cases rare earth element compounds serve as primary luminophores. Thus, Wanmaker and his coworkers [7] have shown the use of lanthanum silicates, activated with cerium, for the preparation of luminophores. During studies of the binary systems of silica with rare earth elements we synthesized and studied lanthanum, yttrium, samarium, and ytterbium silicates, and one of us, together with Galakhov [3, 6], synthesized and studied gadolinium, dysprosium, and erbium silicates, and constructed the phase diagrams of the $Ln_2O_3-SiO_2$ systems (Ln = Y, La, Sm, Gd, Dy, Er, and Yb). The studies have shown similarities in the compositions of the phase diagrams, the existence of three types of chemical compound ($Ln_2O_3 \cdot SiO_2$, $2Ln_2O_3 \cdot 3SiO_2$, and $Ln_2O_3 \cdot 2SiO_2$) in the systems in question, and also the formation of separation regions within wide limits of temperature and concentration. Such similarities are linked to the closeness of the chemical and physical properties of the rare earth elements. This closeness is wholly explainable from the point of view of the similarities of the electronic structures.

EXPERIMENTAL

We studied the pyrochemical, crystallooptical, and x-ray diffraction properties of 12 of the compounds which were obtained. The phase diagrams of the $Sm_2O_3-SiO_2$ and $Yb_2O_3-SiO_2$ systems are shown in Fig. 1 (A, B) and Fig. 2 (A, B). Other systems were discussed in the earlier communications. It was established that in all the systems the 1 : 1 ($Ln_2O_3 \cdot SiO_2$) and 2 : 3 ($2Ln_2O_3 \cdot 3SiO_2$) compounds melted without decomposition. The 1 : 2 ($Ln_2O_3 \cdot 2SiO_2$) compounds in the $La_2O_3-SiO_2$, $Y_2O_3-SiO_2$, and $Sm_2O_3-SiO_2$ systems melt with decomposition into the 2 : 3 ($2Ln_2O_3 \cdot 3SiO_2$) compounds and liquid. In the $Yb_2O_3-SiO_2$ system the 1 : 2 compound melts without decomposition. Partially resorbed crystals of the $2Sm_2O_3 \cdot 3SiO_2$ compound and flat plates of the $Sm_2O_3 \cdot 2SiO_2$ compound, resulting from secondary recrystallization (main background), are shown in Fig. 3. Only crystals of the $Yb_2O_3 \cdot 2SiO_2$ compound can be seen in the microphotograph in Fig. 4. The $2Ln_2O_3 \cdot 3SiO_2$ compounds are stable within a specific temperature range. The stability region for these compounds was established. Their decomposition into the 1 : 1 and 1 : 2 compounds occurs at temperatures from 1600 to 1675°, and the process is reversible. Undecomposed crystals of the $2Sm_2O_3 \cdot 3SiO_2$ compound and also crystals undergoing decomposition can be seen in the microphotograph in Fig. 5.

It is evident from the structural ratios of the compounds in question that they can be represented as follows: $Ln_2O_3 \cdot SiO_2$ as the oxyorthosilicate $Ln_2O[SiO_4]$; $2Ln_2O_3 \cdot 3SiO_2$ as the orthosilicate $Ln_4[SiO_4]_3$; and $Ln_2O_3 \cdot 2SiO_2$ as the diorthosilicate (pyrosilicate) $Ln_2Si_2O_7$. As is known, there are several subgroups, characterized by specific stable electronic configurations, in the rare earth group of elements. Zero, seven, and 14 electrons in the 4f orbital impart stability to the lanthanide ions. There are three stable configurations: La^{3+}, Gd^{3+}, and Lu^{3+}. Ce, Pr, Nd, and Sm belong to the La subgroup; Tb, Dy, and Ho belong to the Gd subgroup; and Er, Tu, and Yb belong to the Lu subgroup. Judging by a number of their properties, yttrium and scandium also belong to the gadolinium and lutecium
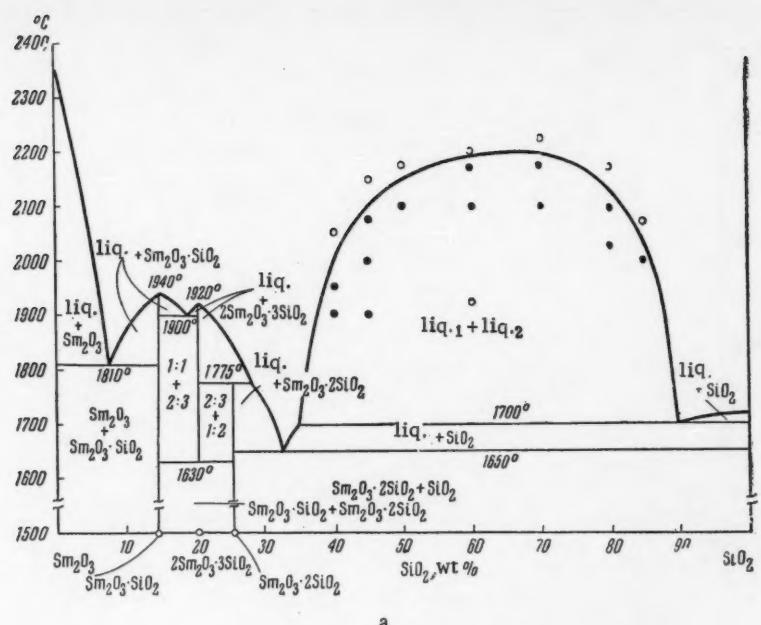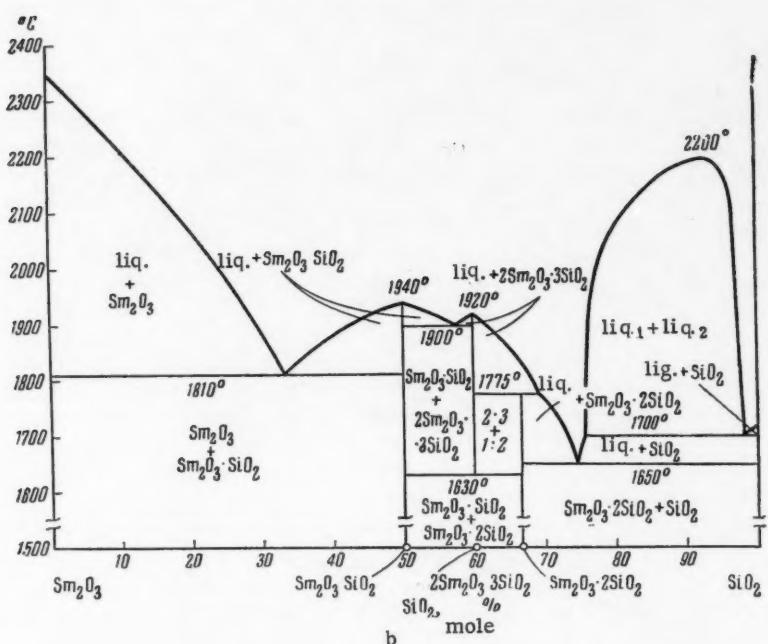
Fig. 1. Phase diagram of the binary system $Sm_2O_3-SiO_2$. A) In wt. %; B) in mole %.
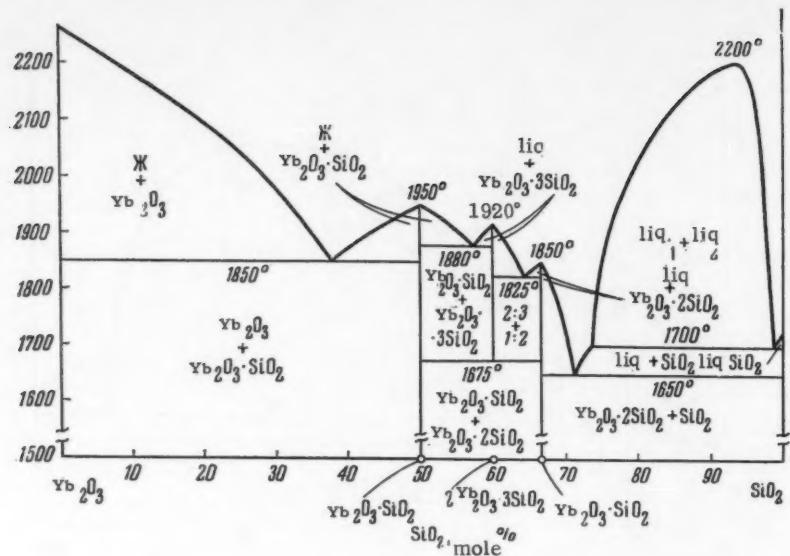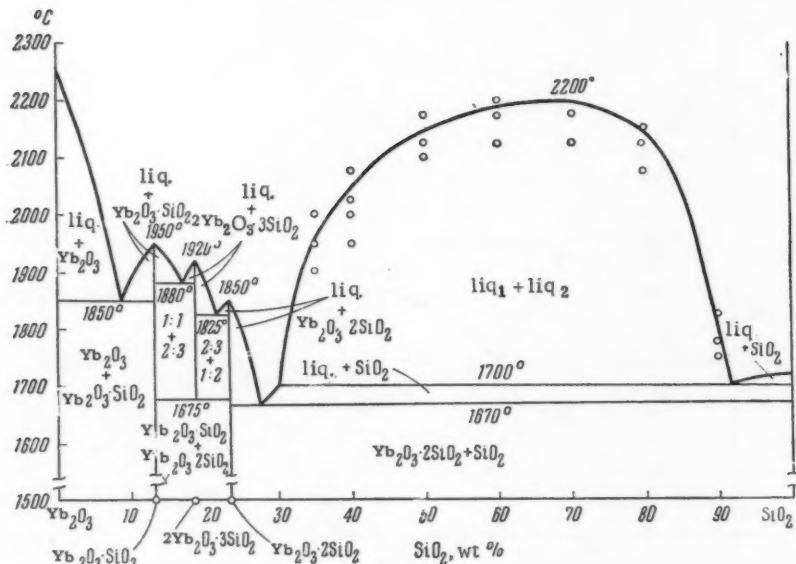
Fig. 2. Phase diagram of the binary system $Yb_2O_3-SiO_2$. A) In wt. %; B) in mole %.

Type of compound	Electronic configuration	M. p. (°C)	Stability limits of the compound (°C)	Refractive indices			Birefringence $n_g - n_p$	Optical axes	Optical sign	Density (g/cm³)
				n_g	n_m	n_p				
Oxyorthosilicates										
$La_2O[SiO_4]$	La^{3+}	1930		1,875		1,855	0,020	Biaxial	(+)	5,72
$Sm_2O[SiO_4]$	La^{3+}	1940		1,885		1,863	0,022	ditto	»	6,36
$Y_2O[SiO_4]$	Gd^{3+}	1980		1,825		1,807	0,018	» »	»	4,49
$Gd_2O[SiO_4]^*$	Gd^{3+}	1900		1,890		1,873	0,017	» »	»	6,55
$Er_2O[SiO_4]^*$	Lu^{3+}	1980		1,825		1,807	0,018	» »	»	
$Yb_2O[SiO_4]$	Lu^{3+}	1950		1,827		1,807	0,020	» »	»	
Orthosilicates										
$La_4[SiO_4]_3$	La^{3+}	1975	1975—1600		1,852	1,837	0,015	Uniaxial	(—)	5,31
$Sm_4[SiO_4]_3$	La^{3+}	1920	1920—1630		1,860	1,840	0,020	ditto	»	5,77
$Y_4[SiO_4]_3$	Gd^{3+}	1950	1950—1650		1,780	1,765	0,015	» »	»	4,39
$Gd_4[SiO_4]_3^*$	Gd^{3+}	1950			1,870	1,855	0,015	» »	»	6,29
$Er_4[SiO_4]_3^*$	Lu^{3+}	1900			1,800	1,780	0,020	» »	»	
$Yb_4[SiO_4]_3$	Lu^{3+}	1920	1920—1675		1,800	1,782	0,018	» »	»	
Pyrosilicates										
$La_2Si_2O_7$	La^{3+}	1750	Melts with decomposition	1,762		1,752	0,010	Biaxial	(+)	4,85
$Sm_2Si_2O_7$	La^{3+}	1775		1,775		1,765	0,010	ditto	»	5,20
$Y_2Si_2O_7$	Gd^{3+}	1775	ditto	1,747		1,737	0,010	» »	»	4,06
$Gd_2Si_2O_7^*$	Gd^{3+}	1720	» »	1,775		1,765	0,010	» »	»	5,33
$Er_2Si_2O_7^*$	Lu^{3+}	1800	Melts without decomposition	1,768		1,740	0,028	» »	»	
$Yb_2Si_2O_7$	Lu^{3+}	1850		1,770		1,740	0,030	» »	»	

* From data supplied by N. A. Toropov, F. Ya. Galakhov, and S. F. Konovalova.

subgroups respectively. The properties of the compounds which have been studied, separated according to the types of these compounds and the types of electronic configuration pertaining to them, are given in Table 1. It is apparent, from Table 1, that a definite dependence of melting point on type of compound was not observed; it should be noted that the melting points of the oxyorthosilicates and orthosilicates are higher than 1900°, and the melting points of the pyrosilicates vary from 1700 to 1850°. Some regularity exists in regard to the optical properties and densities of the compounds.

Thus, for each of the three types of electronic configuration the refractive indices and densities can be seen to increase from La to Sm, from Y to Gd, and from Er to Yb. Besides this, each type of compound is also characterized by its own special features: the densities and refractive indices decrease with change from oxyortho- to ortho- and, finally, to pyrosilicate. Oxyorthosilicates and pyrosilicates are biaxial, optically positive compounds; orthosilicates are uniaxial and optically negative. We were the first to notice a certain peculiarity in the properties of ytterbium pyrosilicate, and with Galakhov were the first to notice this peculiarity in the case of erbium pyrosilicate. Namely, $Er_2Si_2O_7$ and $Yb_2Si_2O_7$ melt without decomposition, whereas all the other pyrosilicates melt with decomposition. Crystals of the two compound in question possess very strong birefringence (0.028-0.030); the birefringence of the other pyrosilicates is uniformly 0.01. According to the magnitude of their birefringence, erbium and ytterbium pyrosilicates somewhat resemble synthetic scandium pyrosilicate, with birefringence 0.04.

This peculiarity of erbium, ytterbium, and scandium silicates can be linked with their belonging to the lutecium subgroup and the phenomenon of the "lanthanide contraction" in the rare earth element series. The eutectic between $Yb_2O_3 \cdot 2SiO_2$ and α-cristobalite, with initial separation of $Yb_2O_3 \cdot 2SiO_2$, is shown in Fig. 6.

The structural similarities of the corresponding compounds of lanthanum and samarium, of gadolinium, dysprosium, and yttrium, and of scandium, erbium, and ytterbium were shown by x-ray data comparisons.

TABLE 2. Compositions and Temperatures of the Critical Separation Points, and the Limiting Compositions of the Liquids Rich in Modifier (Ln_2O_3)

System	Critical point temperature °C	Critical point composition				Temp. at which liquid 1, liquid 2, and α-cristobalite coexist	Composition of coexisting liquid 1 + liquid 2 + α-cristobalite		Ionic radius of Ln (Å)	Limiting composition of liquid rich in modifier (mole% Ln_2O_3)	
		wt.%		mole %			wt.%	mole %		found	calc.
		Ln_2O_3	SiO_2	Ln_2O_3	SiO_2						
La_2O_3—SiO_2	2050	25	75	6,6	94,0	1675	38,2—90 SiO_2 61,8—10 La_2O_3	77 —98 SiO_2 23 — 2 La_2O_3	1,22	23,0	24,5
Sm_2O_3—SiO_2	2200	30	70	6,7	93,3	1700	35—90 SiO_2 65—10 Sm_2O_3	75,8—98,1 SiO_2 24,2—1,9 Sm_2O_3	1,13	24,2	26,3
Y_2O_3—SiO_2	2200	20	80	6,2	93,8	1700	43—95 SiO_2 57—5 Y_2O_3	74,8—98,6 SiO_2 25,2—1,4 Y_2O_3	1,06	25,2	28,3
Yb_2O_3—SiO_2	2200	30	70	6,1	93,9	1700	30—91,5 SiO_2 70—8,5 Yb_2O_3	73,7—98,6 SiO_2 26,3—1,4 Yb_2O_3	1,00	26,3	30,1

It can be assumed that rare earth element silicates form isomorphic mixtures with each other; for a number of the compounds the isomorphism will be complete, for other compounds it is possible that the isomorphic substitution will be incomplete.

More acidic silicates (of the metasilicate type) were not detected experimentally, at temperatures of and above 1600°, in the systems which were studied. Their compositions can be described by the formula $Ln_2(SiO_3)_3$, i.e., it contains 25 mole % Ln_2O_3 and 75 mole % SiO_2. This composition approximately conforms to the composition at which separation begins in the systems (74-77 mole % SiO_2). Apparently, the formation of a separation phase with specific anion structure $(Si_xO_y)^{z-}$, corresponding to the cation coordination type, excludes the formation of metasilicates with another type of structure.

Here the strengths of the $Me-O$ and $Me-Si-O$ bonds are also important. As has been pointed out earlier, there are considerable eliquation regions in the four systems $La_2O_3-SiO_2$, $Y_2O_3-SiO_2$, $Sm_2O_3-SiO_2$, and $Yb_2O_3-SiO_2$ which are bounded in the diagrams by binodal curves.

The compositions and temperatures at which two liquids and cristobalite coexist, the critical separation points, and the limiting compositions of the liquids rich in modifier (Ln_2O_3) are given in Table 2. From Esin's fundamental propositions [8] it ensues that the larger the cation radius, the later does separation begin (when the percent silica in the melt is high).

It is apparent, from comparison of the tabulated data, that La has the largest radius (r = 1.22 A according to Pauling), and separation begins at 77 mole % SiO_2. Then follow Sm, Y, and Yb, for which separation begins at 75.8, 74.8, and 73.7 mole % SiO_2 respectively. This can be qualitatively explained in the following manner: with solution of a metal oxide in SiO_2, when the metal has a strong affinity for oxygen, a small portion of the oxygen ions transfer to the silica. Cybotactic regions develop, closely conforming to the composition of both the metal oxide and also SiO_2. The liquid becomes microheterogeneous and separates. The lower the energy of the reaction between the metal and oxygen, the higher the SiO_2 content of the glass which separates. To a first approximation, it can be assumed to be inversely proportional to the size of the cation. According to Levin and Block [9, 10, 11] it is possible to calculate the limiting separation composition, i.e., the composition of the liquid rich in modifier (Ln_2O_3). In systems which are separating, the following effect is manifest: the composition of one of the phases is close to 100% of the glass-forming material (SiO_2). The second phase can change its composition within certain limits. Consequently, the terms "limiting composition" and "liquid rich in modifier" pertain to the designation of the liquid with a high modifier content. If the small single phase region, adjacent to the pure glass-forming material, is neglected, then the composition of the liquid rich in modifier represents the smallest concentration of modifier necessary for the formation of a stable single phase liquid.

The authors suggest some methods of calculation: an immiscibility equation involving densities (the densities of the limiting compositions of glass-forming material and oxide modifier), and an oxygen-volume method.

Fig. 3. Partially resorbed crystals of $2Sm_2O_3 \cdot 3SiO_2$ and plates of $Sm_2O_3 \cdot 2SiO_2$ (main background), 1800°, × 240.

Fig. 4. $Yb_2O_3 \cdot 2SiO_2$ crystals, 1800°, × 240.

Fig. 5. Decomposition of the $2Sm_2O_3 \cdot 3SiO_2$ compound, 1650°, × 240.

Fig. 6. Eutectic between $Yb_2O_3 \cdot 2SiO_2$ and α-cristobalite, with initial separation of $Yb_2O_3 \cdot 2SiO_2$ crystals, × 240.

For the second method of calculation it is necessary to know the ionic radii of oxygen and the modifier cation, the type of coordination, and the average volume of the space occupied by a close packed oxygen atom. Warren and Pincus defined two types of bond between modifier cations and the oxygen of a tetrahedron (Si tetrahedrally co-ordinates four oxygens). In one type of bond two modifier cations are linked to the same oxygen, with bond-angle approximately 180°. For this type of coordination three of the oxygens in one polyhedron are linked to other polyhedra, and the fourth oxygen is coordinated with the modifier cations. The modifier cation spacing with this type of coordination equals

$$S_g (A) = 2(1{,}40 + M_r^{n+}),$$

<div align="right">(1)</div>

where 1.40 A is the ionic radius of oxygen (Pauling) and M_r^{n+} is the ionic radius of the modifier cation. This type of coordination is designated 'type A'. The second type of bond—'type B'—is characterized by the following situation. In type B coordination each oxygen in the tetrahedral group is unsaturated. Each tetrahedron must be in contact with two modifier cations, in order to neutralize the unsaturated oxygen atoms, since it is physically impossible for one modifier cation to be linked to all four oxygens of the same tetrahedron. In this case the tetrahedron shares a common edge with a modifier polyhedron. The cation spacing in this case can be calculated from the equation

$$S_g(B) = 1{,}154l + 2\sqrt{(O_r + M_r^{n+}) - 0{,}666l^2},$$

(2)

where l = 1.53 for BO_4, and 1.62 for SiO_4.

It is recorded in the articles that in the case of strong modifier cation bonds, greater than 1/4 in the silicate systems (the bond strength is defined as the quotient obtained by dividing the valency by the coordination number, C. N.), type A coordination is obtained. For our systems the bond strength is greater than 1/4 (it equals 1/2 or 3/8), therefore we obtain type A coordination, and the cation spacing is calculated in conformance with Eq. (1).

It was further shown that the cube of the cation spacing corresponds to the volume of glass occupied by one modifier cation. This volume includes: 1) oxygen atoms, 2) glass-forming material cations, and 3) one modifier cation. The volume of the space occupied by an oxygen atom is normally taken to be 17 A^3 (in close packing). The volume occupied by a modifier cation is related to the volume occupied by an oxygen atom as the cubes of the radii:

$$\frac{V_{m.c.}}{17 A^3} = \frac{r^3}{(1{,}40)^3},$$

from which the volume occupied by a modifier cation equals

$$V_{m.c.} = r^3 \cdot \frac{17}{(1{,}40)^3} = 6{,}195r^3.$$

Since the glass-forming material cations are arranged in the spaces between oxygen atoms their volumes are included in the total volume occupied by the oxygen atoms. It is possible to calculate the number of oxygen atoms, N_0, linked to one modifier cation:

$$N_0 = \frac{S_g^3 - 6{,}195r^3}{17},$$

where N_0 is the number of oxygen atoms, S_g^3 is the volume of glass occupied by one modifier cation, and $\underline{r}$ is the radius of the modifier cation.

The oxide formula for the limiting composition of the liquid can be obtained when the number of oxygen atoms is known. In the case of silicate systems, for divalent modifier cations we use the formula

$$RO\left(\frac{N_0 - 1}{2}\right) \cdot SiO_2,$$

for univalent modifier cations

$$R_2O\left(\frac{N_0 - 1/2}{2}\right) \cdot SiO_2,$$
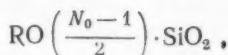
Fig. 7. Eliquation in the $Yb_2O_3-SiO_2$ system, 1850°, ×240.
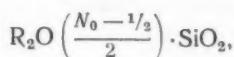
and for trivalent modifier cations

$$R_2O_3\left(\frac{N_0-1,5}{2}\right)\cdot SiO_2.$$

The calculated limiting compositions of the liquids in four systems are given in Table 2. The composition of the eliquation region for the $Yb_2O_3-SiO_2$ system is shown in Fig. 7.

Ol'shanskii and his coworkers [12] derived some rules concerning separation in binary silicate and borate systems. They established that reduction of the immiscibility limits (mole % SiO_2) depended on increase in the ratio of cation radius to valency (r/z), which is confirmed by our data (see Table 2). Glasser, Warshaw, and Roy [13] showed that there was a definite relationship between immiscibility in silicate systems and the properties of the secondary ion. In particular, the authors mention a connection between the immiscibility region and the ionic potential (z/r). Thus, cristobalite appears as the primary phase in the lower separation region when the magnitude of the ionic potential is less than three. The crystalline phase is no longer SiO_2, but is M_xO_y or some kind of silicate when z/r is greater than three. In our studies the ionic potential was less than three and the crystalline phase was silica.

SUMMARY

1. The phase diagrams for the binary systems $Sm_2O_3-SiO_2$ and $Yb_2O_3-SiO_2$ were constructed.

2. The properties of sammarium and ytterbium silicates were studied and compared with the corresponding properties of other rare earth element silicates.

3. The separation region was determined, and the limiting composition of the liquid rich in oxide modifier (Ln_2O_3) was calculated.

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INVESTIGATION OF THE ADSORPTIONAL PROPERTIES
AND SECONDARY POROUS STRUCTURE OF ADSORBENTS,
HAVING A MOLECULAR SIEVE ACTION

COMMUNICATION 3. COMPONENTS OF THE GRANULES OF SYNTHETIC

TYPE A ZEOLITES

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In a previous communication [1], an attempt was made to calculate the limiting amounts of adsorption and the limiting adsorptional volumes from data on the chemical constitution and x-ray structure parameters of the elementary cells of synthetic type A zeolites as cited in the papers of Breck, Read, and others [2, 3]. These authors assumed the following composition for the elementary cells of completely hydrated zeolite A in the sodium (NaA) and calcium (CaA) forms:

Zeolite NaA $\qquad\qquad\qquad Na_{12}[(AlO_2)_{12}(SiO_2)_{12}] \cdot 27\,H_2O$;

Zeolite CaA $\qquad\qquad\qquad Ca_6[(AlO_2)_{12}(SiO_2)_{12}] \cdot 30H_2O$.

According to Barrer, each small cavity of a Type A zeolite contains one occluded molecule of sodium aluminate [4]. Since the windows of the small cavities are not accessible to calcium ions, when the calcium ion exchange form of zeolite A is prepared, the aluminate remains unchanged in the sodium form. Further, ion exchange between Na^+ and Ca^{2+} is scarcely possible for one $NaAlO_2$ molecule isolated in a cavity. Ref. [4] gives the following composition of the elementary cells of completely hydrated crystals of Type A zeolite:

Zeolite NaA $\qquad\qquad\qquad Na_{12}[(AlO_2)_{12}(SiO_2)_{12}]NaAlO_2 \cdot 28.6\,H_2O$;

Zeolite CaA $\qquad\qquad\qquad Ca_6[(AlO_2)_{12}(SiO_2)_{12}]NaAlO_2 \cdot 31.1\,H_2O$.*
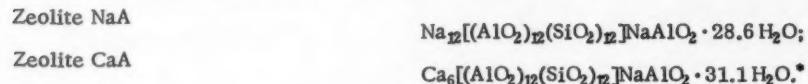
The material subjected to x-ray structure studies [2, 5] were commercial samples of Linde zeolite A. All the authors arrive at notably divergent values for the parameter α of the elementary cubical crystal cells, the deviation lying beyond the limits of experimental error. All this makes it desirable to compare the theoretically calculated adsorptional properties of A zeolites with the data of the various investigators. The method of calculation is explained in detail in the preceding communication. Table 1 gives the results of the calculations for NaA zeolite and Table 2 gives the results for CaA zeolite.

According to Tables 1 and 2 the marked differences in the values of the elementary cell parameters for commercial samples of Linde synthetic type A zeolite crystals as given by various authors, as well as the not completely satisfactory agreement between the compositions of the elementary cells, leads to a noticeable divergence in results of the calculations for d_p, δ_p, and v'_p using these values. However, the limiting amounts adsorbed, a_0, calculated

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* [3] gives 30.4 H_2O for 24.27% water of hydration (results are given of separate analyses with the mean value of 24.27%). This concentration corresponds with 31.1 molecules of H_2O per elementary cell. The value 30.4 H_2O is an error.

TABLE 1. Basic Data on Composition Structure and Properties of Zeolite NaA Crystals

	Breck, et al., [2, 3], 1956	Barrer, et al., [4], 1958	Broussard, et al., [5], 1960
Elementary cell (EC) parameter of the hydrated crystal, α, in A	12.32	12.373 ± 0.003	12.30 ± 0.01
EC parameter of dehydrated crystal, α		12.253 ± 0.003	
Molecular weight of EC of hydrated crystal, M	2191	2302	
Molecular weight of aluminum silicate skeleton of EC, M_c	1704	1786	
Total molecular weight of water hydration in EC, M_{H_2O}	486	515	
X-Ray density of hydrated zeolite, d_p in g/cm^3	1.945	2.066	
Apparent x-ray density of dehydrated zeolite, δ_p in g/cm^3	1.513	1.612	
H_2O concentration in EC of hydrated zeolite, N in %	22.20	22.43	
H_2O concentration calculated per unit mass from dehydrated zeolite, a_0 in mM/g	15.84	16.01	
Limiting adsorbed volume of water calculated as liquid of normal density at 20°, v_0 in cm^3/g	0.286	0.289	
Volume of EC cavities from v_0, v'_p in A^3	803	857	

from the composition of the elementary cells of the zeolite crystals, and the limiting adsorptional volumes, v_0 from the data [2, 4] are not materially different. As a mean value for the limiting adsorptional volume of NaA zeolite we may take $v_0 = 0.288 \pm 0.002$ cm^3/g, Table 1, and for zeolite CaA $v_0 = 0.323 \pm 0.002$ cm^3/g, Table 2. In view of the complete reproducibility of the hydration and dehydration of synthetic Type A zeolites, there is no doubt whatever that the volumes of ordinary liquid water calculated from the composition of the elementary crystal cells actually represents the limiting adsorptional volume.*

Synthetic zeolites are occasionally used in sorption work in the form of powders consisting of crystallites with microscopic dimensions. For gas and vapor adsorption zeolites are used in the form of granules, tablets, or spheres with dimensions of the order of millimeters. The main components of the granules are crystalline zeolite powder and binder. Bentonite type clays are often used as a binder. After mixing the components in the moist state and forming the granules or spheres with subsequent drying, the product is subjected to heat treatment at a temperature ~600° as a result of which the binding properties of the clay show up.

As a result of the packing of the zeolite crystals, in the presence of the binder, spaces are formed in the granules between the contacting crystallites, which represent a secondary porous structure in the granules. The surface of the secondary pores consists of the external surface of the actual zeolite crystallites and the surface of the added binder. The amount of this surface depends on the degree of dispersion of the zeolite crystals and on the properties of the binder after having undergone heat treatment. Actually the zeolite crystals do not appreciably change their porous structure or properties for temperatures up to 700° [2].

If the gas and vapor adsorption by the porous dehydrated crystals themselves is sharply selective because of the molecular sieve action, the adsorption on the surface of the secondary pores is not selective. Therefore, in finding

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* In calculating the limiting adsorptional volumes from the results of sorption measurements the normal density of liquid water is also used.

TABLE 2. Basic Data on Composition Structure and Properties of Zeolite CaA Crystals

	Breck, et al., [2, 3], 1956	Barrer, et al., [4], 1958	Broussard, et al., [5], 1960
Elementary cell (EC) parameter of the hydrated crystal, α, in A	12.26		12.31 ± 0.01
Molecular weight of EC of hydrated crystal, M	2209	2312	
Molecular weight of aluminum silicate skeleton of EC, M_C	1669	1751	
Total molecular weight of water hydration in EC, M_{H_2O}	540	561	
X-Ray density of hydrated zeolite, d_p in g/cm^3	1.990		
Apparent x-ray density of dehydrated zeolite, δ_p in g/cm^3	1.503		
H_2O concentration in EC of hydrated zeolite, N in %	24.4	24.27	
H_2O concentration calculated per unit mass from dehydrated zeolite, a_0 in mM/g	17.97	17.78	
Limiting adsorbed volume of water calculated as liquid of normal density at 20°, v_0 in cm^3/g	0.325	0.321	
Volume of EC cavities from v_0, v'_p in A^3	900		

the properties of the components of the granules, considerable importance attaches to a study of the degree of the dispersion of the zeolite crystals, as well as their adsorptional properties for gases and vapors, for the molecules of which the internal or original porous structure of the constituent dehydrated zeolite crystal granules is both accessible and inaccessible. In the latter case the adsorption will occur only on the surface of the secondary pores of the granules. It is certainly a matter of interest to make an experimental study of the contribution of the actual added binder to the total adsorption by the granules. All these questions constitute the object of the investigations described in the present paper.

EXPERIMENTAL

The materials studied were crystalline samples of Type A zeolites synthesized by various Soviet investigators. The abbreviated symbols for their last names are given in parentheses as follows: I. E. Neimark (Nm), Ya. V. Mirskii (Mr), L. M. Maksimova (Mk), and B. A. Lipkind (Lp). The designation of each sample consisted of the abbreviations of the last name of the author together with the sample number. Samples of American commercial crystalline zeolites Linde 4A and 5A powders were used for comparison. The following sodium forms (NaA) were studied: Nm-300, Nm-347, Mr-275, Mk-90, Mk-1op, Lp-202-2, and Linde 4A. The calcium forms (CaA) were Mr-276 and Linde 5A.

1. In making electron microscope studies of the degree of dispersion of zeolite crystallites, powder samples of Nm-347, Mr-275, Mr-276, and Lp-202-2 were shaken up with water and a drop of the suspension was immediately placed on the slide. After the water evaporated off, a fair number of places could be found where the zeolite crystals were distributed in a single layer. This method did not work for Mk-1op zeolite, since the particles on the slide seem to be strongly aggregated, due apparently to the method of preparation or the surface properties of the powders. Therefore, the Mk-1op zeolite powder was mixed in a film forming solution (1% solution of nitrocellulose in amyl acetate), subjected to careful grinding in an agate mortar to break up the aggregates, and the resulting suspension allowed to form a film on the surface of water. In this film the particles were mainly cemented into one layer, but, apparently, a certain number of the crystallites had been broken up, too. The obvious fragments of crystallites sometimes encountered were not taken into account.

Type of zeolite	Designation	a, $\mu M/g$ at p/p_s			
		0,25	0,50	0,75	1,00
NaA	Nm-300	0,033	0,065	,150	1,46
	Mr -275	0,007	0,045	0,032	0,93
	Mk -90	0,010	0,020	0,027	0,55
	Mky -1оп	0,015	0,018	0,025	0,40
	Linde 4A	0,030	0,055	0,135	1,26
	Nm-242	1,35	1,48	1,67	4,30
NaX	Mk -194	3,58	3,63	3,68	3,95

The photographs were taken on a UÉM-100 electron microscope at 800 magnification. Any further magnification was done optically. Figures 1 and 2 give examples of electron microscope photographs of crystalline zeolite samples which differ by the largest amount in their degree of dispersion. The pictures, particularly Fig. 2, show well formed cubic crystals. The boundary planes of some of the crystals are not oriented parallel with the slide, therefore, in projection they look like rectangles.

A number of the photographs obtained from different parts of the preparations were magnified and subjected to statistical analysis. The results gave curves of the distribution of the number of crystals in percent of the total number studied, as a function of linear dimensions (length of cube edge).

Figure 3 gives the differential curves of the distribution for the zeolite samples synthesized by Soviet investigators. The samples of Neimark (curve 1) and Mirskii (curves 2 and 3) are marked by relatively narrow distribution. The predominant crystal dimensions are near 0.75 μ for Neimark's preparations and 1.2 μ for Mirskii's preparations. Curves 2 and 3 correspond with one and the same zeolite A sample in different ion exchange forms. Since the fact of ion exchange between Na^+ and Ca^{2+} is not reflected in the degree of dispersion of the crystals, the fact that curves 2 and 3 practically coincide shows how good the reproducibility of the parallel experiment is. Maksimova and Lipkind's zeolite samples (curves 4 and 5, Fig. 3) are not only more coarsely dispersed, but they show a considerably wider distribution of the crystals in dimensions. During the granule formation process in packing the crystals, spaces are formed between the contacting crystals, which are proportional to the dimensions of the crystals themselves. Therefore, the degree of dispersion of the zeolite crystals and the nature of the distribution curves, have a decisive effect on the parameters of the secondary porous structure of the zeolite granules.

2. The study of the adsorption on powdered crystalline zeolites of vapors of substances for the molecules of which the primary porosity of the crystals is inaccessible, makes it possible first of all to establish the presence or

Fig. 1. Electron microscope photograph of
NaA zeolite crystals from sample Nm-347.

Fig. 2. Electron microscope photograph of
NaA zeolite crystals from sample Lp-202-2.

TABLE 4. Water Vapor Adsorption Values at 20° for Different Equilibrium Pressures

Type of Zeolite	Designation	a, мM/g at p/p_s					
		0,01	0,05	0,1	0,25	0,5	1,0
NaA	Linde 4A	9,1	10,2	10,6	11,1	11,6	13,0
	Nm -300	9,8	10,8	11,3	11,9	12,5	14,6
	Nm -347	12,2	13,0	13,3	14,1	14,7	—
	Mb -275	12,0	13,1	13,5	14,2	14,8	15,4
	Mk -90	11,6	12,4	13,0	14,0	14,5	16,7
	Mk -1оп	13,0	13,6	14,5	15,3	15,9	16,8
	Lp -202-2	12,0	13,0	13,5	14,0	14,5	15,4
	Linde -5A	8,5	9,3	10,0	10,7	13,3	13,8
CaA	Sr ·276	12,5	14,2	14,7	15,6	16,5	19,5

TABLE 5. Adsorption of Benzene Vapor at 20° on Clay After Heat Treatment at 600°°

	a, мM/g at p/p_s			
	0,25	0,50	0,75	1,00
Clay	0,23	0,35	0,66	1,68
From calculation on the quantity of clay ($\sim 10\%$) contained in zeolite granules	0,023	0,035	0,066	0,168

absence of contamination by aluminum silicate gels, or other zeolites, with larger sized windows leading into the crystal cavities. In the absence of adsorbing contaminants, the adsorption in the small relative pressure region gives an approximate measure of the degree of dispersion of the crystals.

Benzene was chosen as an example of a vapor of this sort. The adsorption isotherm at 20° was taken by the vacuum sorption balance method. The zeolite samples used in the experiments were practically in equilibrium with the atmospheric humidity. This made it possible to take the sample and place the pan and sample into the adsorption tube apparatus without hurrying. Evacuation was carried out for five-six hours at a temperature of 350° to a residual pressure of $\sim 1 \cdot 10^{-6}$ mm Hg. After evacuation the weight loss of the sample was carefully measured, and the amount of completely dehydrated zeolite was calculated, which then served as a basis for calculating the amount of adsorption, referred to unit mass of dehydrated zeolite crystals.

In their general form the benzene adsorption isotherms are no different from the isotherms taken for the granules cited in the first communication [6]. In order to make a more detailed comparison of the adsorptional properties of the different zeolite samples, Table 3 gives adsorption values interpolated from the adsorption isotherms for various characteristic equilibrium pressures.

From the experimental data of Table 3, the sorption of benzene vapor by normal samples of NaA zeolite crystals is very small up to relative pressures not exceeding 0.8. The first four samples are in order of decreasing degree of crystal dispersion. One observes a marked tendency to reduced adsorption on going to more coarsely dispersed zeolite crystal samples. The role of the degree
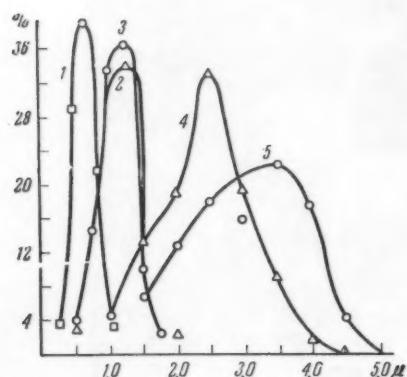
Fig. 3. Differential curves of the distribution of crystals and dimensions for the zeolites: 1) NaA Nm-347; 2) CaA Mn-276; 3) NaA Mn-275; 4) NaA Mk-1op; 5) NaA Lp-202-2.

of dispersion of the crystals appears with a special clarity in the limiting sorption. The smaller the crystal dimensions, the more contacting particles there are per unit mass of the zeolite, and the smaller the spaces between the contacting crystals. Therefore with fine crystals a large volume of voids is filled up by capillary condensation of the benzene vapor.

The Nm-242 sample was prepared at our request under hydrothermal conditions which departed considerably from the optimum for the synthesis of NaA zeolite. It was presumed to contain a considerable admixture of more coarsely porous aluminum silicate gel. No interference lines were observed on the Debye diagrams corresponding with fozhazit.* As a result, the benzene adsorptive capacity of the Nm-242 sample was about 30% of the absorptive capacity of an NaX zeolite with cavities having windows accessible to benzene molecules. For this reason, the Nm-242 sample has lost its clearly marked selective properties.

The Linde 4A zeolite sample was closest to the Nm-300 sample. And, in fact, electron microscope observations on the Linde 4A preparation showed a preponderance of zeolite crystals with dimensions ~ 0.7-$1\,\mu$.

3. In order to make a comparison of the adsorptional properties of crystalline, completely dehydrated zeolites, Table 4 gives values for the adsorption of water vapor interpolated from the adsorption isotherms for various characteristic equilibrium pressures.

From the data of Table 4 the NaA zeolite samples Nm-300 and Linde 4A, are practically identical in their adsorptional properties. The other samples from Soviet investigators show a marked increase in adsorption values. In a previous communication [1], it was shown that the limiting adsorption volume of the calcium form of zeolite A is greater than for the sodium form. By ion exchange between Na^+ and Ca^{2+} in Mr-275 zeolite the Mr-276 zeolite was prepared, with adsorptional properties which are about 10% higher (the calculated limiting adsorbed volumes differ by 12%). The Linde 4A zeolite sample has markedly decreased activity. As a whole, the Type A crystalline zeolites synthesized by Soviet investigators show the good level of adsorptional properties, which is characteristic of a zeolite of this type. The Debye diagrams of the Soviet zeolite samples are identical with the Debye diagrams of the American samples.

4. As an example of a binder we selected a sample of Bentonite type clay, which had been used to prepare the granulated zeolites described in Ya. V. Mirskii's papers. The highly dispersed clay powder was mixed with a small quantity of water, and the resultant plastic mass was dried at a 105° to constant weight and reduced to grains. The resulting grainy product was baked at a temperature of 600° under the conditions usual in the heat treatment of zeolite granules. The weight loss of the clay grains on baking came to 8.56%. The true density of the clay using carbon tetrachloride as pyknometer fluid was found to be equal to 2.43 g/cm³. The adsorption isotherm of benzene vapor on the clay grains was measured on the vacuum sorption balance. Table 5 gives the adsorption values for characteristic equilibrium concentrations.

From the data of Table 5 the adsorption of the clay is approximately an order of magnitude greater than the adsorption of the zeolite crystal powder (Table 3). However, taking into account the amount of clay in the granules (~10%) the level of adsorption values is typical of the benzene adsorption on the surface of the secondary pores of the granules. Here we must keep in mind, that in the granules a part of the zeolite crystal surface is blocked off by the clay in the process of being bound.

In conclusion the authors recognize their pleasant duty of expressing thanks to B. A. Lipkind, I. E. Neimark, Ya, V. Mirskii, and L. M. Maksimov for furnishing them the synthetic zeolite samples to investigate.

SUMMARY
1. Sodium and calcium forms of Type A crystalline zeolites, synthesized by Soviet investigators, differ in degree of crystal dispersion, they contain no nonspecific contaminant adsorbents, and their adsorptive properties are at a level which is typical for zeolites of this type.

2. Use of bentonite type clay as a binder has no substantial effect on the adsorptional properties of the zeolite granules.

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STUDY OF THE ADSORPTIONAL PROPERTIES AND SECONDARY POROUS STRUCTURE OF ADSORBENTS WITH A MOLECULAR SIEVE ACTION

COMMUNICATION 4. GRANULATED SYNTHETIC TYPE A ZEOLITES

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Synthetic zeolites used to adsorb gases and vapor were formed into various shapes. Thus, they may be granules, tablets, or spheres with dimensions of the order of several millimeters. The materials from which the shaped particles are made are highly dispersed crystalline zeolites in powder form together with a binder. Bentonite type clays are often used as binders. The fundamental properties of the initial materials were described in the preceding communication [1]. The present paper presents results of a study of the more important properties of granulated zeolites such as the adsorptivity, the secondary porous structure of the granules, and their apparent engravametric density. The whole concept of the roll of secondary porous structure in adsorption was formulated in one of our preceding communications [2].

EXPERIMENTAL

The objects taken for study were samples of granulated synthetic Type A zeolites prepared by Soviet investigators in the initial stages of the development of their work. These included a series of granulated samples from Ya. V. Mirskii (Mr), during the formation of which the pressure had been changed several times, and one sample of granules from B. A. Lipkind (Lp). The nomenclature of the granulated zeolites consisted of an abbreviation of the author's last name together with a sample number. Linde American granulated zeolites were used for comparison. These consisted of two samples (I) and (II) in the form of $^1/_8$" diameter granules, obtained at different times. *

Among the zeolite granules studied in the sodium form (NaA) were: Mr-296, Lp-202-2, Linde 4A (I) and Linde 4A (II). Representatives of the calcium form (CaA) were the zeolite granules: Mr-297, Mr-347, Mr-372, Mr-380, Linde 5A (I) and Linde 5A (II).

1. Adding binder to the formula for the granules (usually from 10 to 20% in the case of clay) may add to the nonselective component of adsorption, due to the secondary porous structure. This component may be measured by adsorbing the vapor of a substance, the molecules of which will not go through the windows leading into the cavities in the porous structure of the dehydrated zeolite crystals. Benzene [2] is a good compound to use with Type A zeolites.

The vacuum sorption balance was used to measure the sorption and de-sorption isotherms of benzene vapor. The granules were previously degassed at a temperature of 350° to a residual pressure of $\sim 1 \cdot 10^{-6}$ mm Hg. The special features of the method as applied to zeolite have been described previously in Ref. 3.

The general form of the isotherms is no different from those described in the first communication [2]. To find the adsorption on the surface of the secondary pores of the granules, it is only necessary to use the sorption branches of the isotherms. Table 1 gives adsorptions interpolated from the isotherm curves at various equilibrium pressures.

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* The adsorptive property of the I samples were described in the first communication [2].

TABLE 1. Sorption of Benzene Vapor on Zeolite Granules at 20°

Type of zeolite	Designation	a, $\mu M/g$ at p/p_s			
		0,25	0,50	0,75	1,0
NaA	Mr - 296	0,024	0,040	0,074	1,19
	Lp- 202-2	0,027	0,062	0,117	0,81
	Linde 4A (I)	0,023	0,044	0,095	2,45
	Linde 4A (II)	0,050	0,090	0,195	1,51
CaA	Mr - 297	0,030	0,042	0,093	1,70
	Mr - 372	0,010	0,035	0,078	0,55
	Mr - 380	0,010	0,030	0,053	0,61
	Linde 5A (I)	0,023	0,043	0,090	2,38
	Linde 5A (II)	0,040	0,080	0,170	1,75

TABLE 2. Adsorption of Water Vapor on Zeolite Granules at 20°

Type of zeolite	Designation	a, $\mu M/g$ at p/p_s					
		0,01	0,05	0,1	0,25	0,5	1,0
NaA	Mr -296	10,7	11,6	12,0	12,5	13,1	15,4
	Lp -202-2	10,8	12,1	12,6	13,2	13,7	15,1
	Linde 4A (I)	10,5	11,7	11,9	12,4	12,9	17,7
CaA	Mr-297	9,0	10,9	11,3	12,2	13,8	17,9
	Mr-347	7,7	9,4	10,1	11,2	12,4	16,0
	Mr-372	9,6	10,0	10,4	11,3	12,6	14,8
	Mr-380	8,0	8,8	10,3	11,5	12,5	14,9
	Linde 5A (I)	8,8	9,8	10,3	11,0	12,0	15,4
	Linde 5A (II)	8,8	9,6	10,0	10,7	11,5	13,6

For the majority of the zeolite granules studied the sorption at any relative equilibrium pressure over the range 0,25-0,75 does not change more than twofold and is very small. The transition from crystalline zeolite powders to granules, leads to a 2-3 fold increase in the benzene sorption, which is due to the sorptive properties of the binders. At high equilibrium pressures there is capillary condensation of benzene vapor in the secondary porous structure of the granules. The secondary pores consist mainly of voids and spaces between the contacting particles, i.e., between the zeolite crystallites. The denture mass of the granules from forming produces a reduction in volume of the secondary porous structure, part of which forms the capillary condensation volume. This it would seem also causes a reduction in the limiting amount of sorption on granules prepared from crystal powders from approximately the same degree of dispersion, depending on the increase of pressure during granulation.

2. In order to make a direct comparison of the adsorptivities of granulated, completely dehydrated zeolites, the adsorption isotherms of water vapor were measured on the vacuum sorption balance. Table 2 gives the adsorptions interpolated from the isotherms for various equilibrium relative pressures.

The Type NaA zeolite granules studied have practically identical adsorptivities. Almost the same picture, but with a somewhat greater spread in the adsorptions, is observed with CaA zeolite granules. However, the general level values of the adsorption of CaA granules is noticeably less than for NaA granules. We should point out that the Mr-296 granules were prepared from crystalline NaA Mr-275 powder while the Mr-297 granules were prepared from CaA Mr-276 zeolite powder (see [1]).

In turn the crystalline Mr-275 powder was used to prepare the Mr-276 zeolite by ion exchange. With the crystalline Mr-276 zeolite powder (CaA) the adsorptions are approximately 10% greater than for Mr-275 (NaA). With zeolites in granulated form the opposite picture is observed, in spite of the fact that the amount of binder (clay) in the granules is the same in both cases and the methods of preparation are identical. Subsequently, we shall try to explain the fundamental causes of the reduction in adsorptivity of the zeolite CaA granules.

Comparing Table 2 with Table 4 of the third communication [1], it is easy to convince oneself that the Linde 4A and 5A powder zeolites have markedly reduced adsorptivity in comparison with the granulated zeolites prepared by the same firm. Therefore, the level of adsorptivity of the Linde crystalline powder zeolite samples, which we studied previously, is not typical of NaA and CaA zeolites.

3. Two methods were used to study the secondary porous structure of the granules; forcing in mercury and the sorption method. Mercury porimetry makes it possible to find the distribution of the pore volume in the granules according to their effective radii, for a range of radii from $1 \cdot 10^6$ to 15-25 A. From the isotherms for the capillary condensation of the vapor of the substance, the molecules of which can penetrate the porous structure of the actual zeolite crystals (i.e., the primary porocity), it is easy to find the sorption volumes, or the total volumes of pores with effective radii less than 100 A. From these data one can calculate the total volume of the secondary porous structure of the granules.

High and low pressure porometers [4, 5] were used in the mercury impressions studies. The nature of the apparatus was such as to make it possible to carry out successive measurements with one sample of granules in the dilatometer, first with the low pressure porometer (0.08-1.4 kg/cm^2) and then with the high pressure porometer (1.4-1600 kg/cm^2). The zeolite granule experiments were practically at equilibrium with the atmospheric humidity. This made it possible to take the sample for charging the dilatometer at leisure and to determine the moisture content in the granules by complete dehydration. Before filling the dilatometer with mercury the zeolite sample in the dilatometer was carefully degassed at a temperature of 350°. Under these conditions a parallel experiment was being made on dehydrating a second sample of the same granules to calculate the mass of the zeolite granules in the dilatometer when they are completely dehydrated. The technique of making the benzene vapor sorption measurements has been spoken of above.

Fig. 1. Differential porograms of NaA zeolite granules: 1) Linde 4A (I); 2) Mr-296; 3) Lp-202-2. The pore volumes, V, are expressed in cm^3/g in an effective radii of the cylindrical pores, r, are expressed in A.

The mercury impression data served to calculate the differential curves of the volume distribution of the secondary pores of the granules according to their effective radii. In addition, the integral curves of the distributions gave a direct determination of the volumes of mercury V_{Hg} in cm^3/g which are needed to fill the secondary granule pores having effective radii greater than or equal to 50 A. On the other hand, the sorbed benzene volumes, V, are:

$$V_b = av \ cm^3/g, \tag{1}$$

where a mM/g, gives the sorptions interpolated from the sorption branches of the isotherms at the equilibrium relative pressure p/ps = 0.65, corresponding with the volumes of the secondary pores in the zeolite granules having effective radii less than or equal to 50 A [2]. The sums of the volumes

$$V_b = V + V_{Hg} \tag{2}$$

represented the total volumes of the secondary porous structure of the synthetic zeolite granules.

Figures 1 and 2 give examples of the differential curves of the distribution of pore volumes in terms of logarithms of the effective radii (differential porograms) for the most typical zeolite granule samples studied. From a

comparison of the distribution curves of the number of zeolite crystals, according to dimensions (Fig. 3 of Communication 3, [3]) with the curves giving the distribution of pore volumes (Fig. 1) it follows, that a narrow distribution of microscopic zeolite crystals corresponds with a narrow distribution of the volume of the secondary pores formed by the spaces between the contacting crystals (Mr crystal and granule samples). On the other hand, a wider distribution of zeolite crystals also corresponds with a wider distribution of pore volumes (Lp crystal and granule samples). Curve 1 for the distribution of secondary pore volumes of Linde zeolite granules in Fig. 1 is nearer in form to Curve 2 for Mr-296 granules (Fig. 1). Hence, the conclusion may be drawn that the Linde zeolite crystals have a relatively narrow distribution in dimensions compared with Lp-202-2 crystals. Figure 2 gives a larger scale comparison of the differential pore volume distribution curves for Linde 5A (I) and Mr-380 CaA granules. In the present case, the secondary porocity of the Mr-380 granules is more nearly mono-dispersed than the Linde granules.

Fig. 2. Differential porograms of zeolite granules: 1) Linde 5A (I); 2) CaA Mr-380 (V, cm^3/g, r, A).

The principal porogram results and the impressed mercury volumes, V_{Hg}, for the granules studied are given in Table 3.

From the data of Table 3, on going from Mr-297 to Mr-372 granules, i.e., with increase in the pressure under which the granules were formed, the maxima of the porogram curves as well as the regions where the curves start to rise are displaced toward the small pore radius side. The volumes of impressed mercury, V_{Hg}, decrease in the same order. Since, in the initial period of the development of the experiments by Soviet investigators, relatively low pressures were used in forming the granules, the volumes V_{Hg} for the Mr and Lp granules are larger than for the commercial Linde granules.

Table 4 gives the information on the secondary pore volumes of the zeolite granules. It follows from a comparison of the sorbed volumes, V_b, with the impressed mercury volumes, V_{Hg}, that the zeolite granules contain a very small volume of secondary pores having radii less than 50 A.

For the reasons already noted, the total secondary pore volumes of the first granule samples prepared by Soviet investigators, are even greater than for the Linde granules, although for Mr-380 granules the difference amounts to ~10-12%.

DISCUSSION OF EXPERIMENTAL RESULTS

The porous zeolite Type A crystals are definite substances, with, in the dehydrated form, definite apparent densities for each type in ion exchange form. If clays are used as a binder in preparing the granules, i.e., including aluminum silicates, their true densities after heat treatment at 600° are confined to narrow limits and do not differ very much from 2.5 g/cm^3. Therefore, the mean density of the aluminum silicate skeleton of the granules which consists of dehydrated crystals of zeolite and clay, depending on where the granules are produced, is practically constant. However the volume of the secondary porous structure of the granules is different, and it is principally for this reason that the apparent densities of the granules differ. In practical applications, the decisive factor is not the adsorptivity per unit mass of granule, but per unit volume of layer. The latter depends on the gravimetric density of the layer.

In this connection it is a matter of fundamental importance to determine the relationship between the adsorptivities and the apparent density of the zeolite granules on the one hand, and the volume of the secondary porous structure on the other. This problem may be solved if the composition of the zeolite granules and the volume of the secondary pores V_2 are known from experimental data. We shall consider first the calculation of the limiting adsorptional volume of the granules. Let the completely dehydrated zeolite granules contain the fraction γ of dehydrated zeolite crystals, and the fraction $1-\gamma$ of clay, after heat treatment at 600°. According to [1] the limiting adsorbed volumes of water vapor, the molecules of which penetrate both the large and small cavities of the porous crystals, is $v_0 = 0.288 \pm 0.002$ cm^3/g for NaA zeolite and $v_0 = 0.323 \pm 0.002$ cm^3/g for CaA zeolite. If the molecules of other gases and vapors penetrate only the large cavities of the dehydrated crystals, the limiting adsorbed volumes

TABLE 3. Fundamental Constants of the Secondary Porous Structure of Zeolite Granules

Type of zeolite	Designation	Maximum of distribution curve	Region of sharp of distribution curve r_1-r_2, A	V_{Hg}, cm^3/g for $r \geqslant 50$ A
NaA	Mr-296	5000	2000— 6300	0,706
	Lp-202-2	6300	800—25 000	0,463
	Linde 4A (I)	2600	400— 3200	0,295
	Linde 4A (II)	2300	400— 5000	0,277
CaA	Mr -297	5000	2500— 6300	0,660
	Mr -347	4500	2200— 5800	0,403
	Mr -372	2200	1000— 2900	0,387
	Mr -380	3100	1400— 3700	0,352
	Linde 5A (I)	2300	400— 3500	0,314
	Linde 5A (II)	2500	320— 4300	0,275

TABLE 4. Secondary Porous Structure of Zeolite Granules

Type of zeolite	Designation	C_6H_6 a, mM/g at $p/p_s = 0,65$	V_b, cm^3/g for $r \leqslant 50$ A	V_{Hg}, cm^3/g for $r \geqslant 50$ A	$V_z = V_b + V_{Hg}$, cm^3/g
NaA	Mr -296	0,120	0,011	0,706	0,717
	Lp -202-2	0,130	0,012	0,463	0,475
	Linde 4A (I)	0,080	0,007	0,295	0,302
	Linde 4A (II)	0,200	0,018	0,277	0,295
CaA	Mr -297	0,110	0,010	0,660	0,670
	Mr -347	0,092	0,008	0,403	0,411
	Mr -372	0,100	0,009	0,387	0,396
	Mr -380	0,065	0,006	0,352	0,358
	Linde 5A (I)	0,099	0,009	0,314	0,323
	Linde 5A (II)	0,190	0.017	0,275	0,292

will be the fraction α of the values of v_0 given. The quantity α gives the fractional volume of large cavities in the total volume of cavities contained in the elementary crystal cells. From the data [2], α is equal to 0.838 for Type A zeolites and using nitrogen as an example, we obtained limiting volumes of the adsorptional space which are $v_0^i = 0.241$ cm³/g for dehydrated NaA crystals, $v_0^i = 0.271$ cm³/g for CaA crystals. If in preparation of the granules, no conditions are created which exclude a part of the crystals of zeolite from taking part in the sorptional process, the limiting volume of the adsorptional space of the granules of zeolite, v_0^i, will be the γth part of the adsorptional volume of the zeolite crystals in question

$$v_0 = \gamma \overline{v}_0 \tag{3}$$

The apparent density of the granules depends on their composition, i.e., zeolite fraction γ, the apparent density of completely dehydrated zeolite crystals δ and the true density of the binder (clay) $\underline{d}$. From the experimental data [6], the true density of hydrated NaA zeolite crystals containing 22.20% water is 1.990 ± 0.004 g/cm³, and from [7], the value is 2.01 g/cm³ with 22.43% water. Calculating the apparent density of the completely dehydrated NaA crystals from this data leads to the very close values of $\delta = 1.57$ g/cm³ and $\delta = 1.55$ g/cm³. As a mean value for NaA we may take $\delta = 1.56$ g/cm³. We found no data in the literature for a similar calculation of the apparent density δ of CaA crystals. Since the x-ray densities δ_X of dehydrated NaA and CaA crystals are almost the same (1.51 g/cm³ and 1.50 g/cm³ respectively), a proportional value $\delta = 1.55$ g/cm³ may be taken for CaA. The pycnometric value of the true density of clay baked at 600° measured in carbon tetrachloride, and used in Mirskii's experiments was d = 2.43 [1]. These data make it possible to do a calculation on the apparent density of Type A zeolite granules.

TABLE 5. Comparison of Calculated and Experimental Constants of Zeolite Type A Granules

Type of zeolite	Designation	γ	V_g, cm^3/g	δ_g, g/cm^3		Δ, g/cm^3	$\frac{\Delta}{\delta_g}$	v_0', cm^3/g	
				calc.	exp.			calc.	exp.
NaA	Mr-296	0,902	1,335	0,749	0,75	0,475	0,64	0,260	0,26
	Lp-202-2	0,850	1,081	0,926		0,620	0,67	0,245	0,26
	4A (I)	0,900	0,920	1,087	1,08—1,11	0,715	0,66	0,259	0,25
	4A (II)	0,900	0,914	1,094	1,08—1,11	0,706	0,65	0,259	
	4A (I)	0,800	0,902	1,110	1,08—1,11	0,715	0,64	0,230	0,25
CaA	Mr-347	0,947	1,044	0,958		0,624	0,65	0,306	0,27
	Mr-297	0,902	1,293	0,774	0,75	0,492	0,64	0,292	0,29
	Mr-372	0,902	1,019	0,982	1,03	0,667	0,67	0,292	0,25
	Mr-380	0,902	0,981	1,019	1,08	0,688	0,67	0,292	0,21
	5A (I)	0,900	0,944	1,060	1,08—1,11	0,694	0,66	0,290	0,25
	5A (II)	0,900	0,915	1,093	1,08—1,11	0,708	0,65	0,290	0,23
	5A (I)	0,800	0,921	1,087	1,08—1,11	0,694	0,64	0,258	0,25
	5A (II)	0,800	0,890	1,124	1,08—1,11	0,708	0,63	0,258	0,23

We shall assume that the granules contain the fraction γ of zeolite crystals and the fraction $1-\gamma$ of clay after heat treatment at a temperature of ~600°. Then the apparent volume per unit mass of the porous aluminum silicate skeleton of the granules V_c is given by:

$$V_c = \frac{\gamma}{\delta} + \frac{1-\gamma}{d} \, cm^3/g, \tag{4}$$

where δ is the apparent density of completely dehydrated zeolite crystals, and $\underline{d}$ is the true density of the binder in the granules. The apparent volume per unit mass of granules V_g will be equal to the sum of the volumes

$$V_g = V_c + V_2 \, cm^3/g, \tag{5}$$

where V_2 is the experimentally measured volume of the pores of the secondary porous structure. Hence the apparent density of the dehydrated zeolite granules δ_g is given by

$$\delta_g = \frac{1}{V} \, g/cm^3. \tag{6}$$

Table 5 gives a comparison of the calculated and Mirskii's experimentally determined apparent densities of zeolite granules, along with the ratios of the gravimetric densities of the layers of dehydrated zeolite granules Δ to the calculated apparent densities of the granules δ_g. A comparison is also given of the calculated and experimental values of the limiting absorbed volumes on the zeolite granules. Orientational calculations for the American granulated zeolite samples are given for two different compositions of the granules, under the assumption that the binder used is also clay with approximately the same properties. The composition of the dehydrated granules (γ) from the Soviet investigators is calculated from the formula and the humidity of the components making up the mass used in forming the granules.

From the data of Table 5 the calculated and experimental values of the apparent granule densities seemed to be in general and satisfactory agreement. For the Mr and Lp granules, whose formula is known, the ratio of the experimental gravimetric granule layer densities to the calculated apparent granule densities is approximately constant and is $\Delta/\delta_g = 0.66 \pm 0.02$. Thus, the deviation does not exceed $\pm 3\%$. For any granules, the calculated and experimental limiting adsorbed volumes for water vapor are close to one another. However for the majority of the CaA granules, both Soviet and American (in the latter case even for the two different compositions), the limiting adsorbed volumes are less than those calculated from the amount of zeolite crystals in the granules. This deviation comes, as we have noted above, from the relatively greater lowering of the adsorptivity of the granules for water vapor as compared with the adsorptivity of the quantity of crystals per unit mass of dehydrated granules. Apparently, for some as yet unknown reason, part of the highly dispersed zeolite crystals, particularly in the CaA granules, are excluded from the adsorption process. We are going to look into these reasons.

Judging from the ratios of Δ/δ_g in the agreement between the calculated and experimental limiting adsorbed volumes, the amount of binding substance in the Linde granules, may be taken as 10-15%, if it is assumed that the binder is clay. The lower values seem more probable to us.

In conclusion the authors recognize the thanks due to B. A. Lipkind and Ya. V. Mirskii for providing the granulated zeolites for study, as well as the experimental data on the apparent granule densities.

SUMMARY

1. Granulated Type A zeolites prepared by Soviet investigators are identical with corresponding American samples in adsorptivity, both when the adsorbed molecules are able to penetrate the porous structure of the actual zeolite crystals, and when larger molecules are adsorbed only on the surface of the secondary pores of the granules.

2. The zeolite granules studied are substantially different in the volume of secondary porous structures which they possess, which is the principal cause of the difference between the apparent and gravimetric densities of the granulated zeolites, and, in the final reckoning, for their adsorptivities per unit volume of granule layer.

3. The limiting adsorbed volumes, the apparent granule densities, and the gravimetric densities of granule layers, may be calculated from the composition of the granules and the properties of their components.

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THE ADSORPTION ENERGIES OF CO_2, SO_2, $(CH_3)_2CO$ AND $(C_2H_5)_2O$ ON GRAPHITE

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The results of the calculations of the adsorption energies of a series of simple and complex non-polar molecules (Ne, Ar, Kr, H_2, D_2, N_2) and hydrocarbons of different structure, on the basal face of a semi-infinite graphite lattice [1-6] are found to be in good agreement with the experimental values of the heats of adsorption on graphitized carbon blacks. An analogous method, used for the solution of other, similar, problems, i.e., the calculation of the lattice energies of n-alkanes [7] and the compressibility of the graphite lattice [2, 8], also yield values which agree with experimental results.

Over the last few years the heats of adsorption of SO_2 [9] and CO_2 [10] gases on carbon blacks, graphitized by heating, with a homogeneous surface were measured in the Bibi laboratories. In addition, we measured the differential heats of adsorption of $(CH_3)_2CO$ and $(C_2H_5)_2O$ on F1 carbon black (graphitized at a temperature of 3000°). All these materials have fairly diverse properties, differing from the properties of the atoms of inert gases and the molecules of hydrogen, nitrogen and hydrocarbons, the adsorption energies of which were earlier calculated theoretically. Certain of these compounds have constant dipoles [SO_2, $(CH_3)_2CO$ and $(C_2H_5)_2O$]. The CO_2 molecule has a substantial quadrupole localized along the axis. In the present paper the adsorption energy of all compounds on the basal face of graphite has been calculated theoretically, taking into account the special features of their structure in comparison with simple non-polar molecules and hydrocarbon molecules.

The electro-kinetic (dispersion) components of the adsorption energy of an isolated molecule of adsorbate (or its center of forces i) with a cluster of centers of forces j of the graphite lattice (carbon atoms), were calculated with consideration of the electro-kinetic interactions of the type dipole-dipole and dipole-quadrupole. The calculations were analogous to those carried out in earlier investigations by the authors of this paper together with Poshkus [3, 4]. The electrostatic interaction energy Φ_μ of a constant dipole of adsorbate with the induced dipoles in the carbon atoms of the graphite lattice, is described by formula (1) [11]

$$\Phi_\mu = -\Sigma \frac{\alpha_j \cdot \mu_i^2}{2r_{ij}^6}(1 + 3\cos^2\gamma), \tag{1}$$

where α_j is the polarizability of the atom of adsorbent j; μ_i is the dipole moment of the molecule of adsorbate; r_{ij} the distance between the center of the dipole μ_i and the charged center of the atom j; γ is the angle formed by the dipole axis with the direction of the lines r_{ij}. Because there are different values of γ in the case of the interaction of a dipole with a cluster of atoms of the crystalline lattice, then for simplification in the calculation, we use the average value $\Sigma\cos^2\gamma = 1/3$. This average value does not lead to any substantial variation in the value being calculated, because this induced interaction only contributes about 5% of the total value of the adsorption energy. We calculated the repulsive energy Φ_R in the form of an exponential relation with the distance r_{ij}, in a like manner to that in the earlier papers [3, 4].

Thus, the final equation for calculating the energy of interaction of the charged center i of the adsorbate with the charged center j of the graphite lattice took the following form:

$$\Phi_0(z) = -C_{ij1}\sum_j r_{ij}^{-6}(z) - C_{ij2}\sum_j r_{ij}^{-8}(z) - A_{ij}\sum_j r_{ij}^{-6}(z) + B'\sum_j e^{-r_{ij}/\rho_{ij}} \tag{2}$$

TABLE 1. The Structural and Physical Properties of the Molecules of the Adsorbates and Their Charged Centers

Absorbate	Structure of the molecule and the interatomic distances [18]	Dipole moment $\mu_i \cdot 10^{18}$ [19]	Selected positions of the charged centers i	The constants of the separate components of the molecule			
				component	polarizability $\alpha_i \cdot 10^{24}$ cm³ [15]	diamagnetic susceptibility $-\chi_i \cdot 10^{6n}$, cm³	Van der Waals radii r_{0i} A [20]
CO_2	Linear molecule, C—O 1,3 A	—	in the C atom / in the O atoms	C / O	0,96 / 0,84	12,3 [17] / 11,1 [16]	1,7 / 1,6
SO_2	Angle >S 124±5° O, O / S—O 1,45Å	1,6	in the S atom / in the O atoms	S / O	3,0 / 0,84	21,5 [16] / 11,1 [16]	1,8 / 1,6
$(CH_3)_2CO$	Flat molecule, Angles >C 123° O, C / C—C 1,56 A / C=O 1,14 A / C—H 1,09 A	2,75	in the C atoms / in the O atom	CH₃ / C / O	2,26 / 0,96 / 0,84	23,8 [17] / 12,3]17] / 11,1 [16]	2,0 / 1,7 / 1,6
$(C_2H_5)_2O$	Flat "zig-zag" molecule, angles C, C >C 110° O, C, C >O 108° / C—C 1,50 A / C—O 1,43 A	1,18	in the C atoms / in the O atom	CH₃ / CH₂ / O	2,26 / 1,83 / 0,84	23,8 [17] / 18,9 [17] / 11,1 [16]	2,0 / 2,0 / 1,6
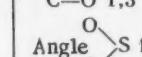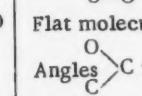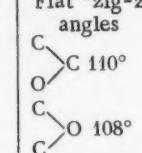
Here Z is the distance of the center i from the plane passing through the center of the carbon atoms j of the outer basal face; r_{ij} is the distance of the center i from the corresponding center of the graphite lattice j; C_{ij1} and C_{ij2} are constants of the dipole-dipole and dipole-quadrupole terms for the electro-kinetic attraction, being calculated by means of the polarizability and magnetic susceptibility of the centers i and j [12, 13, 3, 4]; A_{ij} is the constant of the electrostatic induced attraction of the dipole μ_i to the graphite lattice, equal, according to equation (1) (with $\Sigma \cos^2 \gamma = 1/3$), to the product α_j, μ_i^2. The repulsive constant ρ_{ij} is determined from the corresponding lattice constants ρ_i and ρ_j [3], but the constant B' is found from the condition of equilibrium

$$\left(\frac{\partial \Phi(z)}{\partial z}\right)_{z=z_0} = 0, \tag{3}$$

where the equilibrium distance z_0, determined from the Van der Waal's equilibrium distances in the lattices of i and j, taking into account the relative position of the i atom or molecule over the j carbon atoms of the lattice, is introduced into the interaction energy Φ with the whole cluster of atoms j of the lattice of the adsorbent [3, 4, 8], and not with an isolated atom as in the paper of Barrer [1].

The contribution of the repulsion energy essentially depends on the distance between the interacting charged centers. Thus, for z = 3.7 A the repulsive energy is approximately 31% of the total energy of attraction; in the case where z = 2.9 A it is approximately 40%. In carrying out the present calculation we used the values $\sum_i r^{-6}$, $\sum_i r_{ij}^{-8}$, and $\sum_i e^{-r_{ij}/\rho}$ for different values of z calculated in earlier papers [3, 4, 8]. *

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* In Table 7 of the paper written by the present authors together with Poshkus [4], it is necessary to transpose the positions of the symbols $\underline{b}$ and $\underline{h}$.

TABLE 2. The Values c_{ij1}, c_{ij2}, A_{ij}, and r_e for the Adsorption of Different Materials on Graphite

Adsorbate	Component of molecule of adsorbate	$c_{ij1} \cdot 10^{45}$ kcal. cm^6/mole	$c_{ij2} \cdot 10^{60}$ kcal. cm^8/mole	$A_{ij} \cdot 10^{45}$ kcal. cm^6/mole	r_e, Å
CO_2	C	0,38	0,059	—	3,4
	O	0,335	0,0519		3,4; 3,3*
SO_2	S	0,865	0,089		3,5
	O	0,335	0,0519	0,0345	3,3
$(CH_3)_2CO$	CH_3	0,81	0,139	0,102	3,7
	C	0,38	0,059		3,4
	O	0,335	0,0519		3,3
	CH_3	0,81	0,139		3,7
$(C_2H_5)_2O$	CH_2	0,65	0,113	0,0187	3,7
	O	0,335	0,0519		3,7

* The distance r_e = 3.4 A may be obtained for any position over the graphite lattice, r_e = 3.3 A may be realized only in the case of the disposition of the C atom in the position h, and of the atoms O in the position b.

In general, in order to calculate the interaction energy Φ_0 we followed the method of Barrer [1]; that is, as before, [3, 4, 13] we selected three characteristic positions of the center i over the basal face of graphite from a number of possible positions: over the carbon atom (c), over the center of the distance between two adjacent carbon atoms (b) and over the center of the hexagon (h). Strictly speaking, it should be necessary to consider the probability of molecules of adsorbate being found in different positions with respect to the surface of the adsorbent. However, we determined the value Φ_0 only as the average of the values for those positions which may be attained for molecules of the given configuration. The graphite lattice possesses the peculiarity that the plane disposed at a distance z from the plane x, y, z = 0, passing through the center of the carbon atoms of the basal face is almost equipotential because the maximum difference in the attractive energies for positions c, b and h along this particular plane does not exceed 5% [2]. As a consequence, for molecules, dimensions and configurations such that the distances z of all its centers of forces do not alter with a displacement along the surface of the basal plane (as, for example, for the flat benzene molecule [3, 4]), the differences between the values of the adsorption energies in the positions c, b and h will be insignificant, the energies of adsorption in positions b and h will be similar to the energy of adsorption in the least favourable energy position c (when $z_0 = r_e$, which corresponds to the shortest distance between a component of the adsorbate molecules and an atom of carbon of the graphite lattice equal to the sum of Van der Waals radii of the component of the adsorbate molecule, r_{0i} and of an atom of carbon r_{0j}). But if the surface adsorbs a molecule, the structure and dimensions of which are such that either the whole of it or its separate components, in certain positions with reference to the basal face may be submerged in the cavity between the carbon atoms forming this face so that the appropriate distances of z_0 become less than r_e, then the interaction energy with the lattice will considerably differ depending on the disposition
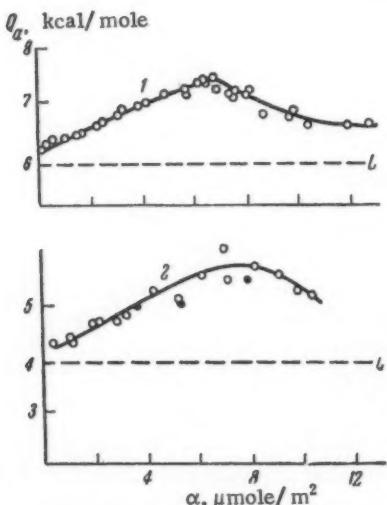
Fig. 1. Relation between the differential heat of adsorption Q_a and the amount adsorbed a of SO_2 (1) and CO_2 (2) gases on carbon black, graphitized by thermal treatment. Here, and on Fig. 2, the horizontal dotted lines are the values of the latent heat of condensation L.

TABLE 3. Calculated Values of Adsorption Energy Φ_0 and Measured Heats of Adsorption Q_0 with the Surface Coverage $\Theta = 0$ (kcal/mole).

Adsorbate	$-\Phi_{0c}$	$-\Phi_{0b}$	$-\Phi_{0h}$	$-\overline{\Phi}_0$	Q_0
CO_2	3,6	3,8	4,9	4,1* 4,5**	4,3
SO_2	5,4	5,7	7,4	6,2	6,1
$(CH_3)_2CO$	7,2	7,6	9,5	8,1	8,0
$(C_2H_5)_2O$	8,4	8,8	11,0	9,4	8,9

* For free movement of the CO_2 molecule with regard to the surface.
** For a localized position of the CO_2 molecule, when the C atom is in position h, but the O atoms are in position b.

Fig. 2. Relation between the differential heat of adsorption Q_a and the amount adsorbed a of $(C_2H_5)_2O$ (1) and $(CH_3)_2CO$ (2) vapours on carbon black, graphitized by thermal treatment.

of the components of the adsorbate molecule i with respect to the surface of adsorbent.*

Orientation of the molecules in the adsorption layer with respect to the basal face of the graphite. In order to calculate the adsorption energy, the values of the distances between the interacting charged centers are of very great importance. Consequently, it is first of all necessary to select a model for the disposition of the molecules of adsorbate on the adsorbent surface which is geometrically the most real and which gives the greatest gain of potential energy. This method of using models proved to be justified in earlier calculations made to obtain the energy of adsorption of normal, branched and cyclic hydrocarbons and an experimental basis was established by the additivity of the heat of adsorption of complex molecules from their components, taking into account the different distances of these components from the surface [3, 4, 14]. Moreover, it was shown that the most energetically favourable distribution of the molecules with respect to the surface leads to values of the areas covered by molecules in a dense monolayer, in agreement with values determined from adsorption results.

The same method in examining models of the possible disposition of molecules of CO_2, SO_2, $(CH_3)_2CO$ and $(C_2H_5)_2O$ was used as in the case of the adsorption of complex hydrocarbon molecules, i.e., we examined the interaction of different charged centers of the molecules of adsorbate with the graphite lattice. Thus, in a molecule of CO_2 we separated three centers of forces, occurring in the centers of the two atoms of oxygen and in the atom of carbon; in a SO_2 molecule there are also three charged centers in the S atom and in the two O atoms; in the $(CH_3)_2CO$ molecule there are four charged centers ($2CH_3$, C and O) and in the molecule $(C_2H_5)_2O$, five centers of forces ($2CH_3$, $2CH_2$ and O). The most favourable energetic distribution for the linear molecule of CO_2 is such that a C atom of radius 1.7 A is in position h and two atoms of O of radius 1.6 A are in position b. If it is assumed that in the case of the charged centers of the CO_2 molecule that it is possible to realize all three positions with respect to the surface, it is then necessary to assume that $r_0 = 1.7$ A for all the molecules because the adsorption energy is insufficient for the deformation of the $C-O$ bond, disposed in parallel to the graphite surface. The non-linear SO_2 molecule may be realized in the three positions c, b and h on the surface by changing position. In addition, for the O atom it is necessary to assume that $r_0 = 1.6$ A because the $S-O$ bond may be slightly inclined in relation to the graphite surface.

The acetone molecule is flat. The Van der Waals' radii of the CH_3 group are equal to 2.0 A, of the central atom of carbon 1.7 A and the oxygen atom 1.6 A. Therefore the flat acetone molecule may not be disposed parallel

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* With the same value of r_e the equilibrium distance z_0 in this case differs for different positions over the graphite lattice. For the position c, $z_{0c} = r_e$, for the position b, $z_{0b} = \sqrt{r_e^2 - 0,25a^2}$ and for position h, $z_{0h} = \sqrt{r_e^2 - a^2}$, where a is a graphite lattice constant [3, 4].

TABLE 4. Calculated Values of the Mutual Energy of Interaction of Adsorbate Molecules Φ_D, Φ_μ, Φ_Q, Φ_R, Φ with the Values of the Area Indicated in Column 2 "Fitting" on the Molecule ω and the Experimental Values of the Increase of the Heat of Adsorption with the Coverage of the Monolayers Equal to $Q_{max} - Q_0$ and Also the Values of the Area $\omega_{Q_{max}}$ "Fitting" on the Molecule with $Q_a = Q_{max}$

Adsorbate	Model of the packing	Φ_D, K_{cal}/M	Φ_μ, K_{cal}/M	Φ_Q, K_{cal}/M	Φ_R, K_{cal}/M	Φ, K_{cal}/M	$\omega_{Q_{max}}$, A^2	$-(Q_{max}-Q_0)$, K_{cal}/M
1	2	3	4	5	6	7	8	9
CO_2	I. 22 A^2	—0,7	—	—1,0	0,3	—1,4	24	—1,5
	II. 18 A^2	—2,4	—	1,2	0,5	—0,7		
SO_2	Free rotation is possible							
	30 A^2	—0,6	—0,1	—	0,1	—0,6	24	—1,3
	Dense layer 20 A^2	—1,9	—0,4	—	0,8	—1,5		
$(C_2H_5)_2O$	53 A^2	—1,0	<—0,1	—	<0,1	—1,0	53	—1,1
	Dense layer 39 A^2	—2,9	—0,1	—	0,6	—2,4		
$(CH_3)_2CO$	31 A^2	—1,0	—1,0	—	0,1	—1,9	32	—1,5

to the surface but slightly inclined, so that all the charged centers of the molecule (CH_3, C and O) will be at the closest distances from it and by the motion of the molecule along the surface each center may establish the energetically favourable positions b and h. Therefore in the case of acetone also, we calculated the energy Φ_0 for each center of CH_3, CH_3C and O for the three positions c, b and h and took the average.

In the diethyl ether molecule the Van der Waals' radii for the CH_3 and CH_2 groups are equal to 2.0 A and for oxygen 1.6 A. But due to the fact that the O atom is in the middle of the molecule its average distance from the surface will also be 2.0 A. Consequently, each center of the $(C_2H_5)_2O$ molecule may establish all three positions with $r_0 = 2.0$ A for all the components of the molecule.

Properties of adsorbates. Because the values of the physical constants were not available for a number of molecules, it was necessary to use those values calculated by an additive method from the appropriate values for the separate components of the molecule.* Table 1 gives the results describing the properties of the adsorbates which we used in the calculation of the adsorption energy. For the carbon atoms of the graphite we used the same constants which were used earlier [3, 4], namely the polarizability $\alpha_j = 0.937 \cdot 10^{-24}$ cm^3 and the diamagnetic susceptibility $\chi_j = 10.54 \cdot 10^{-30}$ cm^3.

Calculation of the energy of adsorption. By using the constants for graphite and the adsorbates given above we calculated the values of the force constants C_{ij1}, C_{ij2} and A_{ij}, given in Table 2, characterizing the interaction between the given centers of the molecules of the adsorbates i and the carbon atoms of the graphite j. In Table 2, the values of the equilibrium distances r_e are also given equal to the sum of the Van der Waals' radii of the carbon atom of the graphite lattice (1.7 A) and the adsorbed molecule or its components i from which, depending on the position, the equilibrium distance z_0 to the plane of the centers of the outer atoms of carbon [3, 4] was determined.

The results of the calculation of the adsorption energy from formula (2) for models representing the disposition of molecules with respect to the basal plane of graphite (referred to above), are presented in Table 3. In the last column of Table 3 the values of the heat of adsorption are also given at zero coverage of the surface Q_0 obtained from Figs. 1 and 2 by extrapolation of the heat adsorption curves up to their intersection with the ordinate axis, i.e., for a surface coverage of $\Theta = 0$.

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* For example, in the case of CO_2 $\alpha_{CO_2} = 2.65 \cdot 10^{-24}$ cm^3 [15], $\chi = -34.6 \cdot 10^{-30}$ cm^3 [16]. Because in the case of an atom of C (in hydrocarbons) $\alpha_C = 0.96 \cdot 10^{-24}$ cm^3 [15] and $\chi_C = -12.3 \cdot 10^{-30} cm^3$ [17], then $\alpha_0 \approx \frac{\alpha_{CO_2} - \alpha_C}{2}$ $= \frac{2,65 - 0,96}{2} \cdot 10^{-24} = 0,84 \cdot 10^{-24}$ cm^3 and $-\chi_0 = -\frac{\chi_{CO_2} - \chi_C}{2} = \frac{34,6 - 12,3}{2} \cdot 10^{-30} = 11,1 \cdot 10^{-20}$ cm^3.

TABLE 5. Calculated Values of the Energy of Adsorption Φ and the Measured Values of the Differential Heat of Adsorption Q_a with Coverage of the Basal Face of Graphite $\Theta \approx 1$, kcal/mole

Adsorbate	$-\Phi$	Q_{max}
CO_2	5,5	5,8
SO_2	7,7	7,4
$(CH_3)_2CO$	10,0	9,5
$(C_2H_5)_2O$	10,4	10,0

As can be seen from Table 3, the calculated values of the adsorption energy of all the molecules, just as for simple non-polar molecules and molecules of different hydrocarbons [3, 4] are found to be in good agreement with the experimental results. The difference between the values of $-\Phi_0$, calculated for two models of the CO_2 orientation is insignificant (0.4 kcal/mole) and is comparable with the variation in the kinetic energy of the molecule—which we are disregarding and which is of the order of magnitude of RT = 0.38 kcal/mole.

Calculation of the mutual interaction energy of adsorbate molecules in a dense monolayer. The mutual interaction potential of adsorbate molecules Φ_{ii} is calculated from the formula

$$\Phi_{ii} = \frac{1}{2}\Sigma\varphi_{ii} = \frac{1}{2}(-C_{ii}\Sigma r_{ii}^{-6} - A_{ii}\Sigma r_{ii}^{-6} + b'\Sigma e^{-r_{ij}/\rho}), \quad (4)$$

where Φ_{ii} is the interaction potential of two isolated centers $\underline{i}$, and r_{ii} is the distance between these centers where the repulsive constant $\underline{b'}$ is found from the equilibrium conditions at the values r_{ii} corresponding to a dense monolayer. In the calculation of the interaction energy the molecule was considered as one charged center sited in its nucleus. For some molecules a calculation was also carried out by dividing the molecule into separate groups (diethyl ether) and atoms (SO_2) in the middle of which charged centers were placed. The divergence in the results of the calculation by these two methods for molecules of such a structure is small (about 10%).* The interaction of the dipoles was calculated approximately by the formula of Keesom, derived by averaging the calculations of all the possible mutual dipole orientations

$$A_{ii} = \frac{2}{3} \cdot \frac{\mu_i^4}{kT}, \quad (5)$$

where μ_i is the dipole moment; $\underline{k}$ is the Boltzman constant; T is the temperature [the calculation was made at T = = 273° for SO_2 and T = 293° for $(CH_3)_2CO$ and $(C_2H_5)_2O$]. Moreover, by considering the mutual interaction of the adsorbate molecules, at least for the CO_2 molecule it is necessary to take into account the interaction of the constant quadrupoles. As shown in the investigations by Drain, Kington and Mcleod [22, 23] this value may have a considerable magnitude. The mutual orientation of CO_2 molecules is important in order to calculate the quadrupolar effect; hence, the maximum attraction of the quadrupole was observed by arranging the molecules as shown in Fig. 3a [23].

We carried out an approximate calculation of the quadrupolar interaction for the molecule 1 with the four adjacent molecules 2, 3, 4 and 5 (Fig. 3a) from the formula [23]

$$\Phi_Q = -\frac{3}{4}Q^2\Sigma r^{-5}, \quad (6)$$

where $\underline{r}$ is the distance between the centers of the molecules, equal to 4.7 A and Q is the quadrupolar moment of the CO_2 molecule equal to $3.2 \cdot 10^{-26}$ e.s.u. [23, 24]. The calculation gave $\Phi_Q \approx -1.0$ kcal/mole. With denser packing of the CO_2 molecules (Fig. 4b) a considerable repulsion of the quadrupoles was observed (up to $\Phi \approx +1.2$ kcal/mole; cf. the work of Kington and McLeod [23]), which leads to a substantial decrease in the interaction energy which supersedes the increase of the dispersion attraction with closer packing. Therefore, in the case of CO_2 molecules, the calculation was carried out for two positions: with a maximum quadrupolar attraction and maximum electro-kinetic attraction (Fig. 3a and b).

For SO_2 molecules the calculation was carried out for two positions: for the case when free rotation is possible and for the densest packing in the monolayer; for the densest packing and the most porous arrangement which corresponds to the area "fitting" on one molecule $\omega = 53.5$ A^2, when $Q_a = Q_{max}$. For acetone, the calculation was carried out for one of the densest arrangements, which also corresponds to $\omega_{Q_{max}} = 32$ A. This correspondence may

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* Due to the configuration of acetone molecules the divergence reaches 30%.

be explained by the presence of a very large dipole moment in the acetone molecule, leading to an intense dipolar interaction and to a dense packing of the molecules.

Table 4 reproduces the results of the calculation of the electro-kinetic energy Φ_D, the electrostatic energy — dipolar (Φ_μ) and quadrupolar (Φ_Q) attraction, repulsive energy (Φ_R), total mutual interaction energy of adsorbate molecules Φ and also the values for the variation in the measured heats of adsorption with a coverage of the monolayer of $Q_{max} - Q_0$ taken from Figs. 1 and 2. Moreover, Table 4 gives the values of the areas "fitting" on a molecule in the monolayer at two different packings, (for each molecule), by which the value of Φ is calculated as well as the experimental value of the area ωQ_{max} "fitting" on the adsorbate molecule at $Q_a = Q_{max}$.
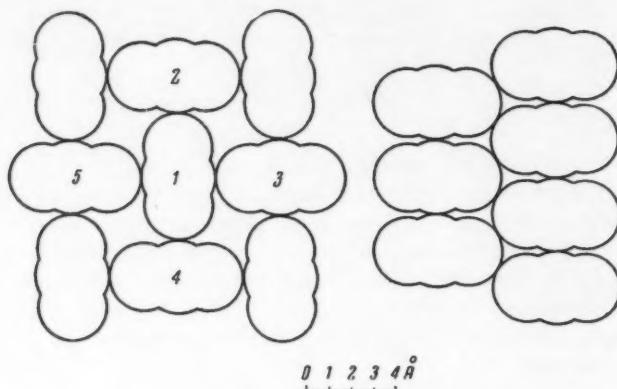
Fig. 3. Plan of disposition of CO_2 molecules: a) With the maximum quadrupolar attraction in the monolayer; b) in a dense monolayer.

From Table 4 it is clear that for CO_2, the values of the interaction energy in the adsorption layer for the model of packing 1 with maximum quadrupolar interaction is in best agreement with the experimental results. The maximum heat of adsorption of diethyl ether corresponds to a comparatively porous coverage of the monolayer when an area of 53 A^2 is necessary for the molecule; the theoretical calculation for this coverage gives good agreement with experiment.[*] Consequently, for further agreement, we selected values of the interaction energy in a dense monolayer for CO_2, SO_2, $(CH_3)_2CO$ and $(C_2H_5)_2O$, equal respectively to —1.4, —1.5, —1.9 and —1.0 kcal/mole.

Table 5 gives the calculated values of the adsorption energies Φ and the measured values of the heat of adsorption Q_a with a coverage of the basal face of graphite $\Theta \approx 1$.

Thus, the calculated values of the adsorption energies of CO_2, SO_2, $(CH_3)_2CO$ and $(C_2H_5)_2O$ at different coverages of the basal face of graphite $\Theta = 0$ and $\Theta \approx 1$ ($\approx \Theta Q_{max}$) are found to be in good agreement with the experimental values of the heat of adsorption on carbon blacks, graphitized by thermal treatment.

SUMMARY

1. The adsorption energies of isolated molecules of different structure have been calculated, i.e., molecules of CO_2, SO_2, $(CH_3)_2CO$, and $(C_2H_5)_2O$, on the surface of the basal face of graphite. The two terms in the potential of the electro-kinetic (dispersion) forces, the potential of the electro-static induction forces and the potential of the repulsive forces were calculated and were found to be close to the values of the differential heats of adsorption on graphitized carbon blacks, measured at small coverages of the surface.

2. The calculated mutual interaction energies of adsorbate molecules for molecules of CO_2, SO_2, $(CH_3)_2CO$ and $(C_2H_5)_2O$ in a dense monolayer for different packings with consideration of the energy of electro-kinetic, electro-

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[*] It is necessary to bear in mind that with $Q_a \approx Q_{max}$ it is possible that the adsorption in the second layer has an effect so that ΘQ_{max} may slightly differ from $\Theta = 1$.

static-dipolar, electrostatic quadrupolar and repulsive interaction forces, are found to be in agreement with the experimental values of the rise in the heat of adsorption with coverage of the monolayer.

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THE ADSORPTION ENERGIES OF WATER, ALCOHOLS,
AMMONIA AND METHYLAMINE ON GRAPHITE

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In the earlier investigations of this series [1-6] calculations of the interaction energies with the graphite basal face of a number of simple and complex non-polar molecules were carried out—in particular, those for numerous hydrocarbons of different structure, and it was established that close agreement was reached between the values of the adsorption potential energy calculated theoretically with values measured by the differential heat of adsorption. In previous work of this series [7] the adsorption energies of a series of other complex molecules [CO_2, SO_2, $(CH_3)_2CO$ and $(C_2H_5)_2O$] possessing constant dipoles or big quadrupoles were calculated. In these calculations, together with the electro-kinetic (dispersion) interaction we also calculated the electrostatic (induced) mutual interaction of adsorbate molecules, where in this case, as well as considering the electro-kinetic interaction, we also simultaneously considered the electrostatic (orientated and quadrupolar) interaction. The values calculated theoretically in both cases for the interaction energy of these molecules with the graphite surface and for the mutual interaction energy of the molecules in the adsorption layer, agreed well with the measured values obtained from the differential heats of adsorption at different coverages.

It would be of interest to calculate the adsorption for those dipolar molecules which are able to develop an even greater mutual interaction of the adsorbate molecules, i.e., to form a hydrogen bond between them. Such adsorbates are for example, water and alcohols, ammonia and amines. The heats of adsorption on graphitized carbon black (mainly obtained by thermal treatment) with a very homogeneous surface, were measured for vapours of NH_3 [8, 9], CH_3NH_2 [8], water [10], normal and branched chain alcohols [10, 11]. In our experimental work [10] it was assumed that in the case of alcohols even with small surface coverages, adsorption does not occur in the form of isolated molecules but in the form of clusters of molecules linked together by hydrogen bonds. An analogous phenomenon may also occur with the adsorption of other molecules, capable of forming hydrogen bonds, in particular, for ammonia and methylamine. In the present work the theoretical calculation of the adsorption energies on graphite was carried out for all these cases.

The additive method of calculation for isolated molecules. The calculation of the adsorption energy of isolated molecules of water, alcohols, ammonia and methylamine was carried out by an additive method [3, 4] on the basis of the physical constants—the polarizability and diamagnetic susceptibility of these molecules or their components i and the atoms of the carbon grating, j and also the structure and Van der Waal's dimensions of the adsorbate molecules and the graphite lattice constants. The calculation was carried out in the same way as before [7] starting from the basic formula

$$\Phi_0(z) = -C_{ij1}\sum_j r_{ij}^{-6}(z) - C_{ij2}\sum_j (r)_{ij}^{-8}(z) - A_{ij}\sum_j r_{ij}^{-6}(z) + B'\sum_j e^{r_{ij}/\rho} \tag{1}$$

where z is the distance of the center of i from the plane x, y, z = 0 passing through the center of the carbon atoms j of the outer basal face, r_{ij} is the distance of the center j from the corresponding center of the graphite lattice, C_{ij1} and C_{ij2} are constants of the dipole-dipolar and dipole-quadrupolar terms of the electro-kinetic attractive energy, calculated by the polarizability α and magnetic susceptibility χ of the centers i and j [3, 4, 12, 13]; $A_i = \alpha_j \mu_i^2$ is the energy constant of the induced attraction of the dipole μ_i, to the graphite lattice [7, 14]; ρ is the repulsive energy exponential constant determined from the corresponding adsorbate and adsorbent constants [3, 4, 13]. The constant B' is found from the condition of equilibrium at the equilibrium distance z_0 of the center i from the plane x, y, z = 0.

TABLE 1. The Physical Properties of Molecules of Adsorbates and Their Groups and the Values of the Constants of Their Electro-Kinetic Attraction to Graphite, C_{ij1} and C_{ij2}

Adsorbate molecule or its group, i	Polarizability $\alpha_i \cdot 10^{24}, cm^3$	Diamagnetic susceptibility $-\chi_i \cdot 10^{30}, cm^3$	r_{oi}, A [20]	$C_{ij1} \cdot 10^{45}$ kcal. cm^6/mole	$C_{ij1} \cdot 10^{60}$ kcal. cm^8/mole
H_2O	1,48 [16]	21,6 [17]	1,4	0,636	0,094
CH_3-	2,26 [16]	23,8 [19]	2,0	0,81	0,139
$CH_2\big\langle$	1,83 [16]	18,9 [19]	2,0	0,65	0,113
$CH-$	1,40 [16]	15,6 [19]	2,0	0,52	0,086
$-C-$	0,96 [16]	12,3 [19]	1,7	0,38	0,059
$-OH$ (in alcohols)	0,97 [16]	18,3 [17]	1,6	0,45	0,060
NH_3	2,46 [18]	27,5 [17]	2,2	0,905	0,152
NH_2-	2,03 [16]	24,3 [17]	2,0	0,793	0,125

In this calculation we used the values $\sum_i r_{ij}^{-6}; \sum_i r_{ij}^{-8}$ and $\sum_i e^{-r_{ij}/\rho}$, calculated for different values of $\underline{z}$ and different positions with respect to the lattice, in the preceeding papers [3, 4, 7].*

Orientation of the molecules of water, alcohols, ammonia and methylamine in the adsorption layer. In general, as in the earlier work [3, 4, 7], we followed the method of Barrer [1] in the calculation of the interaction energy Φ_0 by selecting only three characteristic positions of the center $\underline{i}$ over the basal face of the graphite from numerous possible positions of the adsorbate with respect to the lattice: over a carbon atom (c), over the middle of the distance between two adjacent carbon atoms (b) and over the center of a hexagon (h). Since the difference in energy for these positions is small we then determined the value Φ_0, the average for these positions which may be realized by a molecule of the given configuration. A molecule with a simple configuration (for example, spherical) may be close to the outer carbon atoms of the lattice by the shortest distance r_e (equal to the sum of Van der Waal's radii of the adsorbate molecule r_{0i} and the adsorbent $r_{0j} = 1.70$ A) in all three positions $\underline{c}$, $\underline{b}$ and $\underline{h}$. In this case; for the $\underline{c}$ position $z_{oc} = r_e$, for the $\underline{b}$ position, $z_{ob} = \sqrt{r_e^2 - 0.25a^2}$ and for the $\underline{h}$ position $z_{oh} = \sqrt{r_e^2 - a^2}$, where $\underline{a}$ is the lattice constant of the graphite in the basal plane [3, 4]. The components of the complex molecules may not be sited at the shortest distance r_e from the graphite lattice in all three positions.
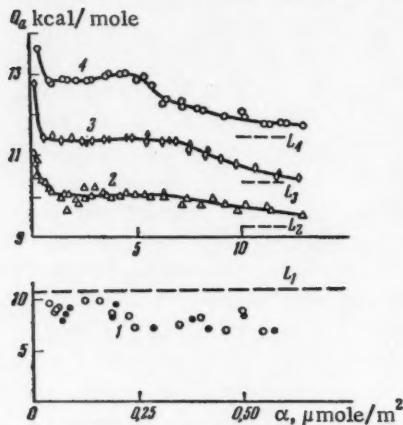
Fig. 1. Relation between the differential heat of adsorption Q_a and α, the amount of water vapour (1), methanol (2), ethanol (3) and n-propanol (4) adsorbed on graphitized channel carbon black. Here, and in Figs. 2 and 3, the horizontal dots are the recorded values of the latent heat of condensation L.

We considered the molecules of water and ammonia as a whole, while we assumed that the charged centers were respectively in the center of the atoms of oxygen and nitrogen and .. : assumed that the molecules of methanol and methylamine consisted of two groups — the CH_3 group and the OH and NH_2 groups respectively. Because the values of r_{0j} for CH_3 and NH_2 are the same (2.0 A, $r_e = 2.0 + 1.7 = 3.7$ A), then the axis of the methylamine molecule is disposed in parallel to the surface. In the case of methanol $r_{0CH_3} = 2.0$ A ($r_e = 3.7$ A), $r_{0OH} = 1.6$ A ($r_e = 3.3$ A), consequently, it was assumed that the CH_3OH molecule is inclined to the surface at an angle. However, in the case of

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* We should bear in mind when using Table 7 given in an earlier paper written by the authors of this paper and Poshkus [4], that it is necessary to transpose the positions of the symbols $\underline{b}$ and $\underline{h}$.

Fig. 2. Relation between the differential heats of adsorption, Q_a and $\underline{a}$, the amount of n-butanol (1), 2-methylpropan-1-ol (2), secondary butanol (3) and tertiary butanol (4) on carbon black, graphitized by thermal treatment.

TABLE 2. The Values of the Dipole Moments μ_i of the Adsorbate Molecules and the Constants of Their Electrostatic Induced Attraction to Graphite A_{ij}

Adsorbate	Dipole moment $\mu_i \cdot 10^{18}$ [21]	$A_{ij} \cdot 10^{45}$ kcal·cm^6/mole
H_2O	1.84	0.0455
Alcohols	1.7	0.0387
NH_3	1.44	0.0285
CHN_3H_2	1.32	0.0234

the remaining normal alcohols, the hydrocarbon chains of which are sited in parallel to the surface, we assumed the same distance as for the CH_3 and CH_2 groups, i.e., $r_e = 3.7$ A, in agreement with the fact that the adsorption energy is insufficient for a substantial deformation of the CH_2-OH bond.

As was shown earlier [3, 4, 15] the complex molecules are arranged in the adsorption layer on the adsorbent surface in such a way that the greatest quantity of their charged centers are found to be at the shortest possible distance from the surface, because this corresponds to the minimum potential energy of all the molecules. We were guided by these considerations in selecting the model of the molecular orientation of isomeric alcohols. Thus we assumed that with the isobutanol molecule (2-methylpropan-1-ol) the CH_3 group, the two CH_2 groups and the OH group are sited at the equilibrium distance z_0 from the surface, but one CH_3 group, (analogous to the corresponding CH_3 group of 3-methylhexane [3,15]) is at a distance of $z_0 + 1.2$ A.

An isolated molecule of secondary butanol may be sited analogously, only in this case, the OH group is sited at a greater distance $z_0 + 0.8$ A from the surface, but all the CH_3 and CH_2 groups are found to be at the same distance z_0. The three CH_3 groups of the trimethyl methanol molecule may be found at the equilibrium distance z_0, whereas the central, quaternary atom of carbon is sited at a distance of $z_0 + 0.5$ A and the OH group is sited at a distance of $z_0 + 1.7$ A.

It was earlier found [3, 4] that the adsorption energy at the equilibrium position, of branched chain hydrocarbons, the groups of which are at different distances from the graphite surface, was found at the minimum of the potential curve constructed from the potential curves of the separate groups taking into account their relative distances. In the case of branched chain molecules of the alcohols the different distances of the separate groups were calculated in an analogous manner but the total energy of the interaction with the lattice was found to be the summarized interaction energies of the separate groups, the values of which were taken from the potential curves of these groups for the corresponding distances $\underline{z}$. The equilibrium distance z_0 was found from the minimum of the potential curve for all the molecules of the isomeric alcohol. This distance was found to be slightly less than the distance $z_{0c} = 3.70$ A for the components of the hydrocarbon part of the normal alcohol molecules. This was due to the fact that at the distance of 3.70 A, the attractive forces of the more distant groups of the isomeric alcohol molecules are not compensated by the repulsive forces. However, the difference in the value of z_{0c} for normal and isomeric alcohols was not great and the value of z_{0c} for the groups of the isomeric alcohol molecules nearest to the surface, varied from 3.68 to 3.65 A.

TABLE 3. Calculated Average Values of the Adsorption Energy Φ for Groups of the Adsorbate Molecules and for These Molecules as a Whole, with a Different Degree of Association β, and Measured Values of the Differential Heats of Adsorption Q_a(kcal/mole) with Different Values of the Differential Heats of Adsorption Q_a (kcal/mole) with Different Coverages of the Surface of the Basal Face of the Graphite

Adsorbate	β	$-\Phi_{C_nH_{2n+1}}$	$-\Phi_{OH}$	$-\Phi_\mu$	Energy of the hydrogen bond [22]	$-\Phi$ ($\beta=1$)	$-\Phi$ ($\beta=2$)	$-\Phi$ ($\beta=\infty$)	Q_0	Q_{max}
H_2O	1,2 / ∞	3,5		0,2	4,5	3,7	5,9	8,2	(7—8)	—
CH_3OH	1,2 / ∞	2,3 / 2,3	2,4 / 1,3	0,2 / 0,1	⎫	4,9	7,9	9,7	10,0	10,0
C_2H_5OH	1,2 / ∞	4,2	1,3	0,1	⎪	5,6	9,6	11,6	11,4	11,4
$n\text{-}C_3H_7OH$	1,2 / ∞	6,1	1,3	0,1	⎪	7,5	10,5	13,5	12,8	13,0
$n\text{-}C_4H_9OH$	1,2 / ∞	7,9	1,3	0,1	⎬ 6	9,3	12,3	15,3	14,1	14,9
$i\text{-}C_4H_9OH$	1,2 / ∞	6,9	1,3	0,1	⎪	8,3	11,3	14,3	12,8	14,1
Secondary C_4H_9OH	1,2 / ∞	8,3	0,8	<0,1	⎪	9,1	12,1	15,1	12,0	13,9
Tertiary C_4H_9OH	1 / 2,∞	7,8 / 6,0	0,5 / 1,3	<0,1 / 0,1	⎭	8,3	10,4	13,4	10,6	14,3
NH_3	1,2 / ∞	2,1		0,1	⎫ 4,0	2,2	4,2	6,2	6,0	6,3
CH_3NH_2	1,2 / ∞	4,6		0,1	⎭	4,7	6,7	8,7	6,5	7,9

The distance between the CH_3 and CH_2 groups in the alcohol molecules is the same as in hydrocarbon molecules. Consequently, these groups may come into contact with the carbon atoms of the basal face of the graphite in the three selected positions c, b and h. We, therefore, carried out the calculation for all three positions and the results were averaged. We also carried out the calculation for the three positions in the case of molecules of water, ammonia and methylamine and then calculated the average result.

The properties of the adsorbates. We used the same constants for graphite as in the earlier work [3, 4], i.e., polarizability $\alpha_j = 0.937 \cdot 10^{-24}$ cm^3 and diamagnetic susceptibility $\chi_j = 10.54 \cdot 10^{-30}$ cm^3. Because the values of the physical constants for the series of molecules and their NH_2 and OH groups were not available it was necessary to use the values of constants obtained from the calculation carried out by an additive method from the corresponding values for separate groups of the molecule.* In Tables 1 and 2 the appropriate results are given.

Calculation of adsorption energy. In Tables 1 and 2 the calculated force constants C_{ij1}, C_{ij2} and A_{ij} are given for the mutual interaction of adsorbate molecules. By using these constants, we calculated the adsorption energy of isolated water molecules, alcohols, ammonia and methylamine (degree of association $\beta = 1$) by using formula (1). Table 3 gives the average values of the total adsorption energies Φ_0 and the separate energy contributions of the hydrocarbon groups $\Phi_{C_nH_{2n+1}}$, the hydroxyl group Φ_{OH} and the induced effect Φ_μ, of the respective molecules to this energy. Moreover, in Table 3 for comparison, the values of the differential heat of adsorption Q are given at small coverages of the surface Θ, obtained from the experimentally obtained differential heat of adsorption isotherms, given in Figs. 1-3, by extrapolation to $\Theta = 0$.

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* Thus the constants α and χ for the OH group in alcohols was found in the following way: $\alpha_{OH} \approx \alpha_{CH_3OH} - \alpha_{CH_3} =$
$= 3.23 \cdot 10^{-24}$ [16] $- 2.26 \cdot 10^{-24}$ [16] $= 0.97 \cdot 10^{-24}$ cm^3; $\chi_{OH} \approx \chi_{H_2O} - \dfrac{\chi_{H_2}}{2} = -21.6 \cdot 10^{-30}$ cm^3 [17] $+ \dfrac{6.6 \cdot 10^{-30}}{2}$ cm^3
[17] $= -18.3 \cdot 10^{-30}$ cm^3. The constant $\chi_{NH_2} \approx \chi_{NH_2} - \dfrac{\chi_{H_2}}{2} = -27.6 \cdot 10^{-30}$ [17] $+ \dfrac{6.6 \cdot 10^{-30}}{2}$ cm^3 [17] $= -24.3 \cdot 10^{-30}$ cm^3.

As can be seen from Table 3, the calculated values of the adsorption energies of the isolated molecules of water, alcohols, ammonia and methylamine are substantially less than the heats of adsorption observed at the very small values of the surface coverage, which are realizable in these experiments. This difference may be connected with the tendency of all these molecules to associate due to the formation of linked hydrogen bonds. Consequently, we also calculated the total adsorption energy of isolated molecules and their association in a cluster of two molecules ($\beta = 2$, when additional energy is required for each molecule, equal to half the energy required for the formation of one hydrogen bond) and a cluster of an infinite number of molecules ($\beta = \infty$, when the energy of one hydrogen bond is required for each molecule).

In this connection, it was necessary to consider in more detail the possible orientation of associated alcohol molecules in the adsorption layer. By using the normal hydrogen bond when the angle of O−H. . . O is about 108° all the alcohol molecules cannot be at the same distance from the surface, certain of their groups must be slightly raised and consequently, the contribution of their dispersion component to the total energy must be less than for molecules, all the groups of which are in direct contact with the surface. We did not have direct results on the orientation of alcohol molecules in the adsorption layer or on the change in the orientation with an increase in the coverage. By studying the crystalline structure of methanol by an x-ray refractive method, Tauer and Lipscomb [23] found that at −160°, i.e., at a very low temperature, the formation of normal hydrogen bonds O−H...O with an angle of about 108° is observed in the CH_3OH crystal. With a higher temperature of −110° another crystalline modification is found, i.e., under these conditions the angle of O−H...O considerably differs from that expected and is approximately equal to 120°, i.e., with an increase of temperature, the chains of the associated molecules of methanol become more planar. This fact led us to the assumption that at the experimental temperature of 20° in the monolayer, in the region of the adsorbent surface, this type of planar packing of associated molecules may be observed not only for methanol (Fig. 4) but also for other normal alcohols. We also took this into consideration in calculating the adsorption energy of the clusters of alcohol molecules. If in fact, the adsorption of alcohols with a big number of carbon atoms in the molecule does diverge from this type of model then it may only lead to a slightly smaller value of their adsorption.

The association of isobutanol occurs in an analogous fashion as that for normal alcohols, because the CH_3 group at the tertiary carbon atom does not impede the formation of chains of associated molecules. In the case of secondary and tertiary butanols, the formation of clusters from an infinitely large number of molecules is sterically not possible but it is possible to form clusters of 3-4 molecules, which increases the adsorption energy of the isolated molecules approximately by 2/3 or 3/4 of the energy of one hydrogen bond. However, we usually calculated the adsorption energy for a degree of association $\beta = \infty$, i.e., we added the energy of one hydrogen bond to the adsorption energy of isolated molecules of these alcohols which was bound to exceed the actual value by 1-1.5 kcal/mole. It should be noted that if an isolated molecule of trimethylmethanol is energetically most favourably sited when the hydroxyl group is at the greatest distance from the adsorbent surface, then in the formation of clusters a reorientation of this molecule must occur: the OH group comes nearer to the surface at the distance of z_0 and one CH_3 group becomes the furthest distance (at a distance of $z_0 + 2.0$ A).


Fig. 3. Relation between the differential heats of adsorption, Q_a and a, the amount of n-butanol (1), 2-methylpropan-1-ol (2), secondary butanol (3) and tertiary butanol (4) on carbon black, graphitized by thermal treatment.


Fig. 4. Plan of the distribution of methanol molecules in an associated adsorption layer.

We took all these factors into consideration in calculating the adsorption energy. In Table 3, our calculated values of the total adsorption energy Φ are given for water, alcohols, ammonia and methylamine with different degree of association. These values are compared with both the heat of adsorption Q_0 for a surface coverage of $\Theta \to 0$ and with the values of Q_{max}, i.e., with the maximum values of differential heats of adsorption of these vapours on graphitized carbon black observed to be near to the completion of the dense monolayer (with $\Theta \approx 1$).

From Table 3 it is clear that the best agreement between the theoretically calculated values of Φ and the measured heats of adsorption are found by considering the formation of clusters.

It is necessary to note that these theoretical values of the adsorption energies of alcohols are approximate, because we did not have available reliable values of the energy of the hydrogen bond and we used the same value of 6 kcal/mole for all the alcohols. Moreover, to obtain a more definite comparison between the theoretical calculations and experiments it will be necessary in future by using methods of statistical thermodynamics, to calculate the possible energy contributions at a given temperature of the different clusters in the monolayer and the possibility of a reorientation of these molecules as well as a gradual superimposition of polymolecular adsorption.

SUMMARY

1. The adsorption energy of water, normal and isomeric alcohols, ammonia and methylamine molecules on the surface of the basal face of graphite has been calculated. In the calculation, the two terms in the potential of the electro-kinetic (dispersion) forces and the potential of the electrostatic (induced) attractive forces have been considered and the potential of the repulsive forces has been calculated in the form of its relation with the distance.

2. The values of the adsorption energies of isolated molecules of water, alcohols, ammonia and methylamine are significantly less than the measured heat of adsorption. Calculation of the energy of association of these molecules in the adsorption layer and using the energy of formation of hydrogen bonds, led to agreement between the calculated values of the adsorption energy and the heats of adsorption.

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THE CATALYTIC EFFECT OF WATER ON THE CHEMICAL
REACTION BETWEEN OXIDES AT HIGH TEMPERATURES

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During high-temperature synthesis of oxidic materials water vapor, always present in the furnace atmosphere, is adsorbed by the oxide particles and exerts a catalytic effect on the physicochemical reactions which occur in them. Water vapor is also a catalyst in many heterogeneous catalytic reactions [1-3]. However, the mechanism of the catalytic effect of water has been insufficiently studied. The effect of water vapor on the kinetics of the chemical reactions of the oxides MgO, CaO, BaO, and ZnO with Al_2O_3, and of CaO with quartz and amorphous silica, and also on the crystallization and agglomeration of some of the oxides, is studied in the current work.

EXPERIMENTAL

"Analytically pure" quality chemical reagents—magnesium, calcium, and barium carbonates, zinc oxide, aluminum hydroxide, amorphous silicon dioxide, and quartz (rock crystal)—were used as raw materials. Mixtures of powdered oxides were ground in an agate mortar and briquetted under a pressure of 500 kg/cm^2. The experiments were carried out in a tubular platinum furnace, in a vacuum of 1 mm Hg, and in an atmosphere of oxygen with different partial pressures of water vapor. An atmosphere with a given water vapor content was produced by passing the oxygen over water heated to a suitable temperature [4]. Dry oxygen (p_{H_2O} = 0.1 mm) was obtained by passing the oxygen through phosphorus pentoxide and sulphuric acid (sp. gr. 1.84). The experiments were carried out in an atmosphere of pure oxygen, and not in air, in order to exlude a possible effect of the nitrogen and carbon dioxide contents of air on the reaction rate.

The specimens were initially heated in vacuum, and the required atmosphere was created on attainment of the experimental temperature. The chemical compounds in the oxide mixtures, after heating, were quantitatively determined by chemical phase analysis. For analysis of the products from a MgO + Al_2O_3 mixture the free MgO was dissolved in 10% (nominal) NH_4NO_3 solution with heating; $MgAl_2O_4$ and Al_2O_3 remained in the residue. For analysis of the products from a ZnO + Al_2O_3 mixture [5] the ZnO was selectively dissolved in 1 : 1 hydrochloric acid solution at room temperature; $ZnAl_2O_4$ and Al_2O_3 remained in the residue. The dissolved components were determined by complexometric titration [6]. The products from CaO + Al_2O_3, CaO + SiO_2, and BaO + Al_2O_3 mixtures were analyzed by the ethyl glycerate method [7, 8], based on the dissolving of free lime (or barium oxide) in a hot mixture of dehydrated glycerin and absolute alcohol with subsequent titration, against an alcoholic solution of ammonium acetate, of the calcium (or barium) glycerate which was formed. The phase composition of the reaction products was also determined with the aid of x-ray analysis by the powder method, with copper radiation through a nickel filter, in a Debye chamber, and by an ionization method. The experimental results are given in Table 1.

As is evident from Table 1, in all the heated mixtures the lowest oxide reactivities were observed when the heating was carried out in a vacuum (1 mm); the reactivity increased in dry oxygen (p_{H_2O} = 0.1 mm), and intensified with increase in partial pressure of water. The MgO + Al_2O_3 mixture was prepared from oxides which had been previously calcined at 1300° for two hours. The reaction of the mixture was studied at temperatures of 1150, 1250, and 1300°, to which they were exposed for one hour. The amount of MgO which combined approximately doubled with change in the partial pressure of water vapor from 0.1 to 355 mm. A more spectacular effect of water vapor was observed for the reaction of CaO with Al_2O_3, as is evident from the series of experiments following No. 4. The effect of the gas phase composition was manifested particularly strongly also in experiments Nos. 5 and 6. With partial pressure of water vapor 355 mm and duration 20 min the amount of combined CaO equalled 87%, whereas in vacuum for duration 240 min only 81.5% of the CaO reacted. The duration of the experiments differed by a factor of twelve in the comparable experiments.

TABLE 1. The Catalytic Effect of Water Vapor on the Chemical Reaction between Oxides in Solid Phases

Expt. No.	Composition of mixture	Temp. (°C)	Duration (min)	vacuum of 1mm	Amount of combined MeO*, %			
					atmosphere of oxygen with water vapor content (mm) (quartz)			
					0,1	17,5	92,5	355
1	MgO+Al$_2$O$_3$	1150	60	7,7	8,5	10,5	15,5	18,0
2	MgO+Al$_2$O$_3$	1250	60	16,8	18,0	26,0	32,8	38,0
3	MgO+Al$_2$O$_3$	1300	60	24,1	25,5	37,0	46,0	52,1
4	CaO+Al$_2$O$_3$	1250	60	52,5	68,5	85,0	89,0	96,0
5	CaO+Al$_2$O$_3$	1250	20					87,0
6	CaO+Al$_2$O$_3$	1250	240	81,5				
7	CaO+SiO$_2$ (quartz)	1200	60	39,6	48,2	56,7	58,6	62,4
8	CaO+SiO$_2$ (amorphous)	1000	60	34,7	46,5	59,2	67,5	75,5
9	CaO+SiO$_2$ (amorphous)	1000	20	23,5				58,2
10	CaO+SiO$_2$ (amorphous)	1000	240	59,4				
11	BaO+Al$_2$O$_3$	1250	60	40,0	64,0	80,0	84,0	92,0
12	BaO+Al$_2$O$_3$	1250	20					88,0
13	BaO+Al$_2$O$_3$	1250	240	80,0				
14	ZnO+Al$_2$O$_3$	1000	60	13,0	16,5	28,4	39,4	54,2

* MeO denotes MgO, CaO, BaO, or ZnO, according to the system under consideration.
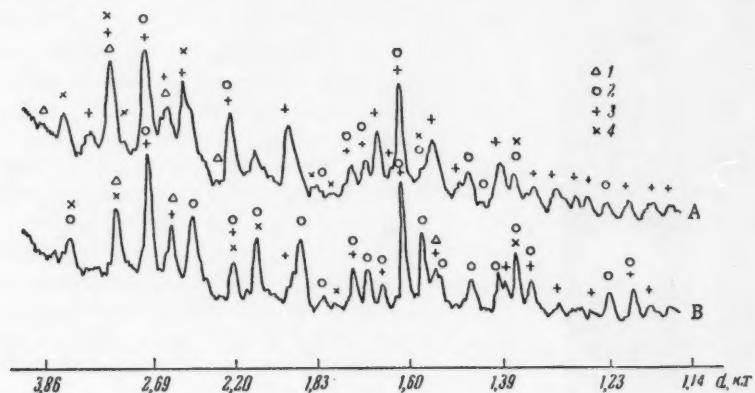
Fig. 1. X-ray diffraction curves of CaO + Al$_2$O$_3$ mixtures heated under different conditions: A) 1250° for 20 min, p_{H_2O} = 355 mm, amount of combined CaO equals 87%; B) 1250° for 240 min, in vacuum (1 mm), amount of combined CaO equals 81.5%. 1) CaO · Al$_2$O$_3$; 2) 3CaO · Al$_2$O$_3$; 3) 5CaO · 3Al$_2$O$_3$; 4) 3CaO · 5Al$_2$O$_3$.

The formation of 3CaO · Al$_2$O$_3$, CaO · Al$_2$O$_3$, and insignificant amounts of 5CaO · 3Al$_2$O$_3$ and 3CaO · 5Al$_2$O$_3$ was observed for the CaO−Al$_2$O$_3$ system in the temperature range 1000-1300° [9]. X-ray analysis of the heated CaO + Al$_2$O$_3$ mixtures showed that the amount of chemical compounds formed depends on the composition of the gaseous atmosphere. Detailed analysis of the x-ray diffraction curves (Fig. 1) showed that mainly 3CaO · Al$_2$O$_3$ and CaO · Al$_2$O$_3$, and an insignificant amount of 5CaO · 3Al$_2$O$_3$ were formed when the mixture was heated in vacuum and in dry oxygen. In moist oxygen (p_{H_2O} = 355 mm) the predominant phase, equally with CaO · Al$_2$O$_3$, was 5CaO · 3Al$_2$O$_3$, and a small amount of 3CaO · Al$_2$O$_3$ was formed. As is evident from the experiments in question, water selectively catalyzes the reactions of the CaO + Al$_2$O$_3$ mixture.

The catalytic effect of water vapor was dissimilar during the reactions of CaO with quartz and with amorphous silica. Rock crystals, ground in an agate mortar until it would pass through a 0.05 mm mesh screen, was used as the

TABLE 2. Agglomeration of Magnesium Oxide, Heated at 1500° for One Hour

Agglomeration	Atmosphere	
characteristic	air	hydrogen
Linear contraction (%)	7.2	18.0
Volumetric wt. (g/cm^3)	2.13	3.21
Specific wt.	3.56	3.58
Apparent porosity (%)	39.85	9.63
True porosity (%)	40.10	10.20
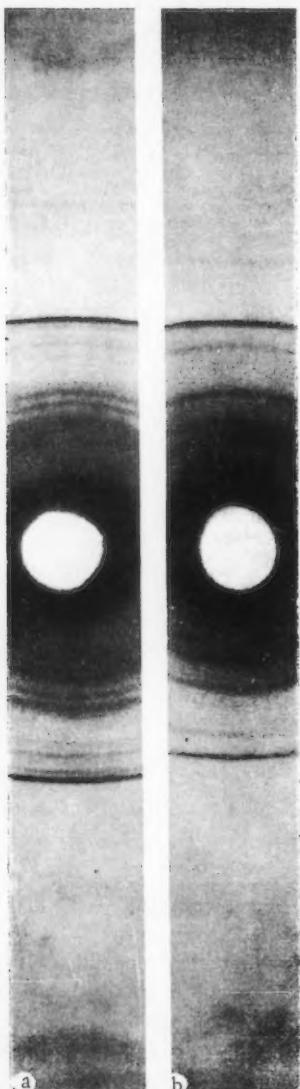
Fig. 2. X-ray photographs of alumina specimens heated at 950° for one hour. A) In moist oxygen ($p_{H_2O} = 17.5$ mm); B) in dry oxygen ($p_{H_2O} = 0.1$ mm).

raw material in the experiments with quartz. The amount of combined CaO increased from 48.2 to 62.4% with change in the partial pressure of water vapor from 0.1 to 355 mm (Table 1, experiment No. 7). Dehydrated silicic acid, calcined at 500°, was used as amorphous silica. Because of the high reactivity of the CaO + amorphous SiO_2 mixture the experiments were carried out at 1000° for one hour (Table 1, experiments Nos. 8-10). The amount of combined CaO increased from 46.5 to 75.5% with change of p_{H_2O} from 0.1 to 355 mm.

It is evident, from comparison of the experiments with quartz and with silicon dioxide, that the catalytic action of water vapor increases with increase in dispersion (specific surface area) of the powdered oxide. The reaction rates in BaO + Al_2O_3 and ZnO + Al_2O_3 mixtures also increased with increase in partial pressure of water vapor in the gas phase (Table 1, experiments Nos. 11-14).

We also studied the action of water vapor on the crystallization and agglomeration of the oxides. Specimens of alumina, prepared from Al(OH)$_3$, were heated at 950° for one hour in moist oxygen ($p_{H_2O} = 17.5$ mm). For comparison, similar specimens were heated at the same temperature for the same time in dry oxygen ($p_{H_2O} = 0.1$ mm). X-ray photographs of the specimens showed that low-temperature γ-Al_2O_3 was formed in dry oxygen, but more intensive crystallization of alumina occurred with the formation of $\varkappa$- and γ-high-temperature modifications in moist oxygen, as is evident from Fig. 2. The refractive indices of the heated specimens of alumina, measured with the aid of a polarizing microscope, amounted to n = 1.678 (heating in moist oxygen) and n = 1.638 (heating in dry oxygen). Water vapor also catalyzes the agglomeration of the oxides. Specimens of silicic acid measuring $3 \cdot 7 \cdot 30$ mm, compressed under a pressure of 500 kg/cm^2, were heated at 1000° for one hour. The specimens contracted by 12% in moist oxygen, and by 7.0% in dry oxygen. It was further shown that water vapor catalyzes the agglomeration of oxides also at higher temperatures. Thus, when specimens of magnesium oxide were heated at 1500° for one hour, the linear contraction in moist oxygen was 10.7%, but in dry oxygen, under the same conditions, the linear contraction was 7.2%.

DISCUSSION OF EXPERIMENTAL RESULTS

The experiments in question showed that water vapor, present in the gas phase, increases the reactivity of the oxides, and intensifies the crystallization and agglomeration of the oxides at high temperatures. The catalytic action of water vapor is accomplished by dint of its chemical adsorption on the oxide surfaces. The atoms become polarized, as a result of the introduction of hydroxide groups into the oxide lattice, weakening the bonds in the surface layers of the crystal. The greater the disturbance of the stoichiometry of the crystalline lattice, the higher the reactivity of the material, and the more the mobility of the atoms in the lattice increases [10, 11].

The emergence of a transitional active state (t.a.s.) of the chemical compound surface is another factor increasing

TABLE 3. Effect of the Gaseous Atmosphere on the Course of the Reaction $MgO + Al_2O_3 = MgAl_2O_4$

Temp. (°C)	Duration (min)	Amount of $MgAl_2O_4$ formed (%)	
		in air	in hydrogen
1150	30	11.8	41.0
1200	60	47.2	93.0

Fig. 3. The reaction between quartz and Co_3O_4. Duration 30 min. (According to Hedvall and Schiller.)

the reactivity of the oxides with adsorption of water vapor. The experimental data shows that the t.a.s. is of great importance in the kinetics of many physicochemical processes. The nature of the t.a.s. can be seen most clearly in dissociation processes and during phase changes in oxides. We studied the conditions under which the t.a.s. emerges.

We studied [12, 13] the effect of the gaseous atmosphere on the agglomeration and the agglomerating recrystallization of oxides (CuO, Fe_2O_3, Cr_2O_3, MgO, and TiO_2) at high temperatures. The maximum agglomeration and agglomerating recrystallization activation is observed when the partial pressure of oxygen in the gas phase equals the dissociation pressure of the oxide. A t.a.s. of the material, in which it possesses increased reactivity, emerges under these conditions. For example, magnesium oxide agglomerates more intensively in hydrogen than in air, as is shown in Table 2.

The effect of the gaseous atmosphere on the recrystallization of magnesium oxide was studied by exposing the material to a temperature of 1750° for two hours. The crystals were small, not exceeding 24 μ, when the specimens were heated in air, but attained 160 μ when the specimens were heated in hydrogen. The spinel-forming reaction proceeds more intensively in hydrogen than in air, as is evident from Table 3. The intensified course of the spinel-forming reaction, agglomeration, and growth of magnesium oxide crystals in hydrogen is explained by the emergence of a t.a.s. of magnesium oxide, because the oxygen pressure, established in the hydrogen atmosphere, is commensurable with the dissociation pressure of magnesium oxide, the magnitude of which is $1.4 \cdot 10^{-6}$ atm at 1750° [14].

Hedvall [15] showed that during phase changes in solids the reactivity of the material increases (Hedvall effect). Thus, for example, the reaction between cobaltosic oxide (Co_3O_4) and quartz ([15], p. 187) accelerates in certain temperature ranges, as is evident from Fig. 3. The first acceleration of the reaction is brought about by $\beta \rightleftharpoons \alpha$ change of the quartz at 575°, and the second, beginning at 800°, is brought about by the dissociation $Co_3O_4 \rightleftharpoons 3CoO + 1/2 O_2$. The Hedvall effect also depends on the emergence of a t.a.s. of the material.

The t.a.s. emerging during polymorphic changes and during dissociation processes in oxides is characterized by the maximum development of the exchange of atoms between the equilibrium phases, which corresponds to the maximum development of anharmonic vibrations of the molecules in the material [16-18]. Many changes in the properties of the materials depend on this phenomenon: increase in heat capacity, diffusion rate of the atoms, and reactivity. The circumstance that the material can exist in a t.a.s. for as long a time as is desired, if the conditions necessary for the existence of the t.a.s. (temperature, pressure, and concentration) are maintained, is very important in chemical kinetics. Depending on the external conditions, the whole body, or only its surface atoms, or the surface chemical compounds and individual complex groups, formed with foreign molecules or atoms adsorbed from the gaseous atmosphere or from solution, can exist in the t.a.s. Because of these characteristics t.a.s. can appear in a variety of reactions: in solid phase reactions, in heterogeneous catalysis, and in solution and gas reactions.

A t.a.s. also emerges when water is chemically adsorbed on oxides. The resulting surface chemical compounds exist in equilibrium with the gas phase. The equilibrium is dynamic. Maximum activation is attained when the dissociation pressure of the surface chemical compounds equals the partial pressure of the water vapor in the gas phase and the free energy of transformation (association $\rightleftharpoons$ dissociation) is zero ($\Delta F = 0$). Because of the heterogeneity of the energy of the chemical adsorption centers, the resulting surface chemical complexes have different dissociation pressures. Therefore, in the case of chemical adsorption, the t.a.s. can emerge in wide ranges of temperature and partial pressures of water vapor, as was also observed in the described experiments.

SUMMARY

1. The catalytic effect of water vapor on the reactions of the oxides MgO, CaO, BaO, and ZnO with Al_2O_3, on the reactions of CaO with quartz and with amorphous silica, and also on the crystallization of alumina and on the agglomeration of silica and of magnesium oxide, was established.

2. A transitional active state theory is described, explaining the increase in reactivity of oxides during dissociation processes and during the course of polymorphic changes.

3. The catalytic effect of chemically adsorbed water on physico-chemical processes in oxides (chemical reactions, agglomeration, and agglomerating recrystallization) is explained by the emergence of a transitional active state of the surface chemical compounds.

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PHYSICAL AND CHEMICAL PROPERTIES
OF WS$_2$ CATALYSTS

COMMUNICATION No. 6. PORE STRUCTURE AND CHEMICAL COMPOSITION
OF AN UNMIXED WS$_2$ CATALYST

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In our previous work [1, 2] it was found that an unmixed WS$_2$ catalyst may contain not only excess non-stoichiometric sulfur, but also excess nonstoichiometric tungsten.* The relation between the atomic ratio of S : W in the catalyst and its phase composition, crystal structure, and activity was established in this work. At the same time, up to now to relation has been established between the pore structure of an unmixed WS$_2$ catalyst and its chemical composition over a wide range of S : W and likewise there are no detailed data on the change in these properties during the operation of the catalyst. To fill this gap therefore, in the present work we used the low-temperature adsorption of N$_2$ and, for some examples, the adsorption of toluene or benzene to study the pore structure and chemical composition according to elementary analysis data on the W, S, C, and H contents of various samples of unmixed WS$_2$ catalyst with S : W ratios in the range of 2.30-1.53. The samples included unused catalysts, catalysts that had been used in destructive hydrogenation, and also catalysts that had been treated in vacuum at 400° or with solvents at room temperature.

EXPERIMENTAL

All the WS$_2$ catalyst samples investigated were described in previous communication [1-3].** The unused and untreated samples 1, 3, 4, and 5 and samples 10, 12, and 14, which had been used under various conditions in industrial destructive hydrogenation of oils under a pressure of H$_2$, were obtained by decomposition of various batches of (NH$_4$)$_2$WS$_4$ at 400° by the method described in detail in [4] and [5]. Samples 15 and 16 were the center and thin surface layer, respectively, of tablets of sample 14. Samples with the subscript 400 were pumped out in high vacuum to constant weight at 400°.*** Sample 13$_{400}$ was obtained from sample 12 by treatment with a large excess of benzene at room temperature for a week with subsequent pumping out in high vacuum at 400°; sample 9$_{20}$ was obtained from sample 3 by treatment at room temperature with a tenfold amount of CS$_2$ (two weeks) and C$_2$H$_5$OH (ten days) successively with subsequent pumping out at room temperature to a residual pressure of $8 \cdot 10^{-6}$ mm Hg.

The adsorption of nitrogen vapor at the boiling point of liquid nitrogen was measured with quartz spring balances after preliminary outgassing of the catalysts. The pore volume V was calculated from the saturation point, the specific surfaces S from the BET equation ($\omega_0 = 16.2$ A^2), and the most probable effective radius r_{eff} (without allowance for the thickness of the adsorption film) from the Kelvin equation. The methods used for measuring and calculating the adsorption of N$_2$ were completely analogous to those described in [3]. Figures 1-4 show N$_2$ adsorption isotherms, characteristic curves of A = f(r_{eff}), where A is the amount of nitrogen adsorbed, and the pore volume distribution with respect to the effective radius for samples 1$_{400}$, 4$_{400}$, 5$_{400}$, 10$_{400}$, 12$_{400}$, 13$_{400}$, 14$_{400}$ and 15$_{400}$.

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* By excess tungsten or sulfur we mean not free elementary W or S, but excess of these elements with respect to the stoichiometric formula WS$_2$.

** Detailed data on the chemical composition are given for the first time in the present work for a series of samples studied in [1, 2], including all the samples with S : W < 2.

*** The samples were heated in vacuum directly in the adsorption apparatus before determination of the N$_2$ adsorption isotherm.

Parallel experiments were carried out to determine the reproducibility of the adsorption data: for samples 4_{400} and 5_{400}, two different catalyst samples of each were studied and for samples 4_{400}, 5_{400}, 12_{400}, 14_{400}, and 15_{400}, the adsorption of N_2 on each sample was remeasured after the sample had been pumped out again at 400°. Figure 1-3 show that the reproducibility of the results was quite satisfactory in all cases. For samples 1, 3, 10, and 12, we used
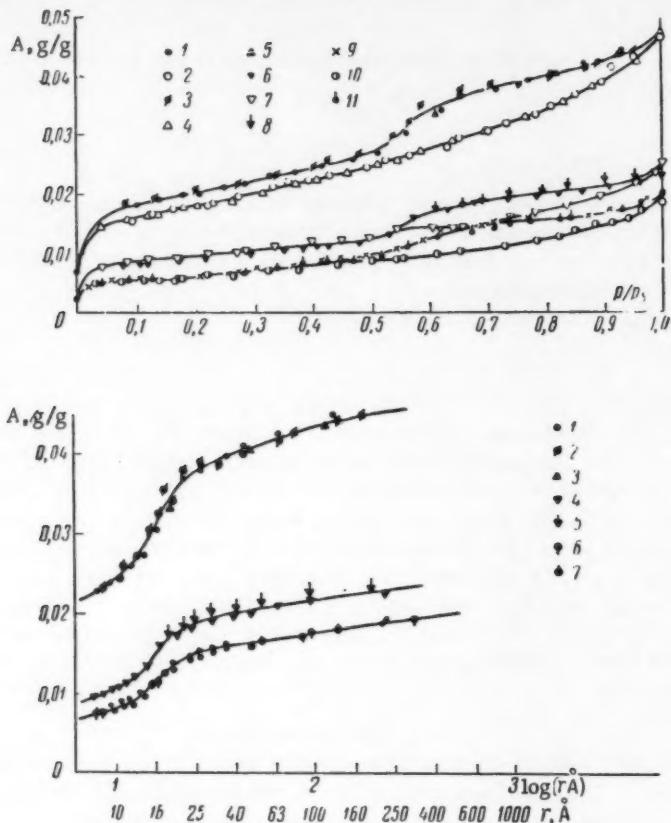
Fig. 1. Nitrogen vapor adsorption isotherms at the boiling point of liquid nitrogen and characteristic curves of WS_2 catalysts: 1) Sample 4_{400}; 2, 3) 4_{400} (after 1 and pumping out at 400°; 4, 5) 4_{400} (parallel experiment with a different sample); 6) 15_{400}; 7, 8) 15_{400} (after 6 and pumping out at 400°); 9) 14_{400}; 10, 11) 14_{400} (after 9 and pumping out at 400°); (the black points represent desorption).

a method described previously [6] (from the change in refractive index) to determine the adsorption of toluene from an isooctane solution at room temperature and calculated the specific surface of the WS_2 catalysts ($\omega_0 = 50\ A^2$ [7]). In this case the catalyst samples were not given any special preliminary treatment before the measurement. After the first adsorption experiment, all the samples used were pumped out in high vacuum at 400° and then used for the second experiment etc. Isotherms of the adsorption (X−solid line) and total content (A−broken line) of toluene in the adsorption volume for samples 1, 1_{400}, 3, and 10_{400} are shown in Fig. 5; this figure shows that the adsorption power of the samples studied in the second experiment was appreciably greater than in the first experiment and then hardly changed in subsequent experiments (see, for example, sample 1). It is evident that the pores of the catalysts were cleaned by the action of the toluene−isooctane solution in the first experiment and the thermal treatment in vacuum and this will be discussed in detail below.

The numbering of the WS_2 catalyst samples used in the second and subsequent experiments on the adsorption of toluene corresponded to the numbering of samples used for the adsorption of nitrogen. As the solvents extracted

both sulfur compounds and coking products from the catalyst pores while thermal treatment in vacuum removed only sulfur compounds, beginning with the second experiment on the adsorption of toluene, the unused sample 1 was denoted by 1_{400} and the used sample 12 was denoted by 13_{400}.[*] With this numbering, samples 1_{400} and 13_{400} were analogous in properties to the corresponding samples used for the adsorption of nitrogen. As regards the used sample 10, in analogy with sample 12, this sample should have been denoted by a different number beginning with the second experiment on the adsorption of toluene as it differed from sample 10_{400} on which the adsorption of nitrogen was carried out in the same way as sample 13_{400} differed from sample 12_{400}. However, because of the insignificant content of coking products and to simplify the numbering, catalyst 10 used both for the adsorption of nitrogen and for the adsorption of toluene was denoted as the same sample 10_{400}.
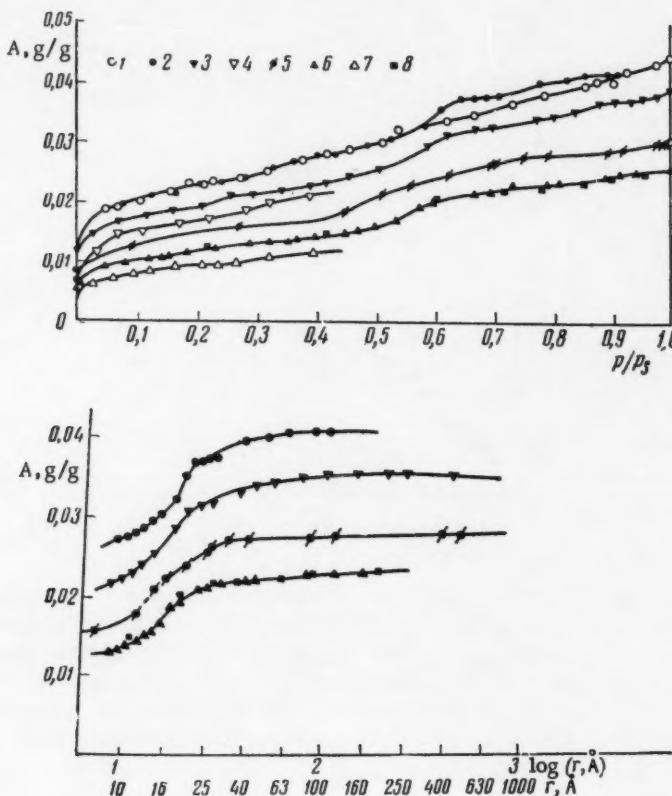
Fig. 2. Nitrogen vapor adsorption isotherms at the boiling point of liquid nitrogen and characteristic curves of WS_2 catalysts: 1, 2) sample 1_{400}; 3) 10_{400}; 4) 10_{400} (after 3 and pumping out at 400°); 5) 13_{400}; 6) 12_{400}; 7, 8) 12_{400} (after 6 and pumping out at 400°); (the black points represent desorption).

Figure 6 shows that for sample 12, there was an increase in the refractive index of a solution with a low toluene content during adsorption in the first experiment; with an increase in the toluene concentration in the solution, only the value of X increased. Consequently, in this experiment the change in the refractive index was determined pri-

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[*] In denoting sample 12 in the second and subsequent experiments as sample 13_{400}, we assumed that benzene and the toluene−isooctane solution cleaned the pores of sample 12 to the same extent and this was confirmed by the good agreement in the values of S for sample 13_{400} obtained from the adsorption of nitrogen and toluene (see below). Only the first experiment was carried out with sample 3.

marily by the elution from sample 12 of hydrocarbons previously adsorbed on the catalyst during destructive hydrogenation, whose refractive index was close to the intersection of the line of X with the abscissa axis, i.e., close to 1.44. Therefore, the value of X for the starting sample 12 was calculated conditionally (in [cc(ref. ind.)]/g) and it was impossible to determine the specific surface of sample 12 by the liquid-phase method. It is noteworthy that beginning with the second experiment, i.e., after the removal of adsorbed hydrocarbons, for this sample we obtained a quite satisfactory adsorption isotherm and the specific surface calculated from it hardly differed from that determined from N_2 adsorption for sample 13_{400} (see table).
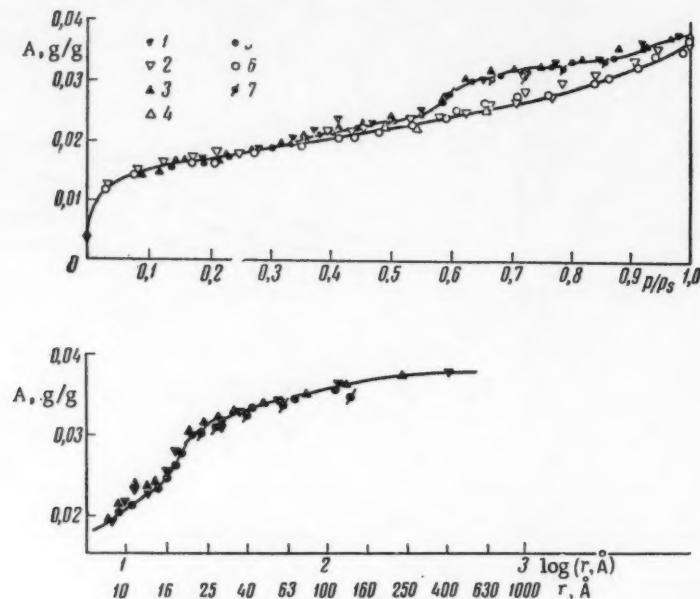
Fig. 3. Nitrogen vapor adsorption isotherm at the boiling point of liquid nitrogen and the characteristic curve for two portions of sample 5_{400}: portion 1 (in succession): 1) desorption, pumping out at 400°; 2) adsorption; 3) desorption, pumping out at 400°; 4) adsorption; portion 2 (in succession); 5) desorption, pumping out at 400°; 6) adsorption; 7) desorption; (the black points represent desorption).

The specific surface of samples 1_{400} and 9_{20} and also the pore volume of sample 9_{20} were calculated from the adsorption of benzene at 20° ($\omega_0 = 40$ A^2), determined by the dynamic method of Rubinshtein and Afanas'ev [8, 9] and shown in Fig. 7 in the coordinates of the BET equation.* The pore volumes and specific surfaces of these samples are given in the table, which shows that when the pores and surface of the WS_2 catalyst were freed from impurities (sample 1_{400} pumped out at 400° and sample 13_{400} washed with benzene and pumped out at 400°), all the methods used for determining adsorption gave similar values for the specific surface. An analogous conclusion may be drawn for pore volumes if we compare the values of V and S determined by the dynamic method for sample 9_{20} (sample 3 washed with CS_2) with corresponding data for sample 3_{400} pumped out at 400° (V = 0.057 cc/g and S = = 66 m^2/g), determined by the low-temperature adsorption of N_2 [1]. The difference in the specific surface for samples 10_{400} determined from the adsorption of nitrogen and toluene is explained by the different preliminary treatments of the corresponding samples, which are only conditionally given the same numbers, and will be discussed in detail below.

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* The dynamic method was found to be unsuitable for determining the specific surface of WS_2 catalysts with a high acidity and a high content of excess sulfur without preliminary treatment (for example, samples 1 and 3).

Pore Structure and Chemical Composition of WS$_2$ Catalysts

Sample No.	Pore volume cc/g (on N$_2$)	Specific surface, m^2/g determination method		Content, wt. %				Atomic ratio S : W
		vacuum BET(onN)	liquid phase (onC$_6$H$_5$CH$_3$)	W	S	C	H	
Unused								
1			42	67,84	26,92	0,83	0,47	2,27
3			42	64,02	25,65	0,44	0,69	2,30
4	0,004 **	8 **		68,12	22,83	0,11	0,37	1,92
5				67,13	25,92	1,16	0,46	2,25
Used								
10				66,41	24,83	1,26	1,04	2,14
12				68,23	24,63	3,20	0,53	2,08
14				69,40	22,47	4,43	0,32	1,86
15				66,84	23,98	2,84	0,39	2,06
16				64,45	21,35	4,77	0,67	1,90
Pumped out in vacuum								
1$_{400}$	0,055	65 (58)	60					
4$_{400}$	0,059	49		74,79	20,00	0,31	0,16	1,53
5$_{400}$	0,048	50						
6$_{400}$	0,051	54		71,46	25,33	0,63	0,22	2,03
7$_{400}$	0,036	23		72,25	24,78	0,50	0,18	1,97
8$_{400}$	0,003	3		72,93	25,02	0,36	0,11	1,97
9$_{20}$	(0,063)	(64)		73,61	25,17	0,71	0,20	1,96
10$_{400}$	0,048	46	60 ***			1,32	0,61	
12$_{400}$	0,033	31				3,40	0,47	
13$_{400}$	0,039	40	39	66,62	23,19	2,55	0,44	2,00
14$_{400}$	0,025	17						
15$_{400}$	0,030	27						

* Values determined by the dynamic method from the adsorption of C$_6$H$_5$ are given in brackets.

** The pore volume and specific surface of sample 4 were determined after pumping out at 20°.

*** In comparison with sample 10$_{400}$ used for the determination of nitrogen adsorption and the chemical composition, sample 10$_{400}$ on which the adsorption of toluene was determined was additionally treated with toluene—isooctane solution at room temperature.

The chemical composition of the samples studied was determined in the analytical laboratory of the Institute of Organic Chemistry, to whose workers we are very grateful, and are given in the table together with the atomic ratio S : W calculated from these data. The W, S, C, and H were determined gravimetrically on one sample by combustion in a stream of O$_2$. The sulfur oxides were absorbed with silver, the CO$_2$ with ascarite, and the H$_2$O with anhydrone. The tungsten was determined as WO$_3$. The elementary composition of each sample was calculated as the mean from several parallel determinations. The accuracy of the determination of W, S, C, and H was checked by comparing the results of analyzing three portions of sample 3 ground to different extents. The mean absolute errors of the determination were ±0.30, 0.12, 0.09, and 0.02 wt. %, respectively, i.e., the determinations were made with quite satisfactory accuracy. Nitrogen was absent from all the samples studied as was established by Dumas analysis.

DISCUSSION OF EXPERIMENTAL RESULTS

According to the data in the table, a peculiarity of the chemical composition of a WS$_2$ catalyst is the fact that the tungsten and sulfur contents generally differ from the values corresponding to stoichiometric WS$_2$ and the WS$_2$ catalyst may contain not only excess sulfur, but also excess nonstoichiometric tungsten (unused sample 4 and used sample 14). To determine the pore structure of a WS$_2$ catalyst with excess nonstoichiometric tungsten, we studied the adsorption of nitrogen at liquid nitrogen temperature on untreated sample 4 with an atomic ratio S : W = 1.92

after preliminary outgassing under mild conditions, namely, in high vacuum at $20°$, to constant weight, which did not change after 4 hr. The specific surface and pore volume of sample 4_{20} obtained in this way were found to equal $8 \ m^2/g$ and 0.004 cc/g, respectively. At the same time, these samples were considerably higher (49 m^2/g and

Fig. 4. Pore volume distribution of WS_2 catalysts with respect to the effective radius calculated from nitrogen vapor desorption isotherms: 1) Sample 4_{400}; 2) 15_{400}; 3) 14_{400}.

Fig. 5. Isotherms of the adsorption (X) of toluene from a solution in isooctane at room temperature on the starting WS_2 catalysts (first experiment) and catalysts pumped out at $400°$ (subsequent experiments): 1) Sample 1 (first experiment); 2) 3 (first experiment); 3) 1_{400} (second experiment); 4) 1_{400} (third experiment); 5) 1_{400} (fourth experiment); 6) 10_{400} (second and subsequent experiments). The broken lines show the total toluene content in the adsorption volume (A).

0.059 cc/g) for sample 4_{400} pumped out at $400°$. In comparing these data it should be noted particularly that a considerable amount of sulfur was liberated from sample 4 when it was heated to $400°$ as the tungsten and sulfur contents of sample 4_{400} corresponded to the formula $WS_{1.53}$. Thus, the pores of a WS_2 catalyst with excess tungsten obtained from $(NH_4)_2WS_4$ and not treated in any way were filled with sulfur or compounds of it, which were removed readily by thermal treatment in vacuum. We drew an analogous conclusion previously in [3] for a catalyst with S : W > > 2, but this conclusion is of particular interest in the present case as it refers to a WS_2 catalyst with a sulfur content lower than the value corresponding to the stoichiometric formula WS_2. It is also noteworthy that there was a sharp decrease in the acidity of the WS_2 catalyst with excess tungsten during thermal treatment as was established previously in [2] for sample 4 and was evidently connected with the liberation of sulfur or compounds of it from the pores. The considerable content of excess nonstoichiometric tungsten in sample 4_{400} is also noteworthy. Nonetheless, the excess tungsten did not form an independent crystalline phase in sample 4_{400} as x-ray diffraction patterns of 4_{400} obtained in a standard camera with a diameter of 57.3 mm (Co-K radiation, 27 kv, 12 ma, Agfa Laue-film, exposure 10 hr) appeared to coincide completely with x-ray diffraction patterns of sample 3 obtained previously with Co-K radiations in [1].

A comparison of the chemical composition of sample 4_{400} with the composition of samples obtained from catalysts with excess sulfur by thermal treatment in vacuum or treatment with solvents (samples 3_{400} with S : W = 2.006 and 9_{20} obtained from sample 3, sample 13_{400} obtained from sample 12, and samples 6_{400}, 7_{400}, and 8_{400} obtained from samples 6, 7, and 8 with S : W of 2.16, 2.08, and 2.05 respectively) shows that WS_2 catalysts with excess tungsten or sulfur differ in the composition of the "rigid skeleton" which is not broken down by moderate thermal treatment. Only the excess sulfur was removed readily from catalysts with S : W > > 2 and therefore the "rigid" skeleton of catalysts with S : W > 2 is close in composition to the stoichiometric value. At the same time, the excess tungsten was not removed from catalysts with S : W < 2 by thermal treatment and consequently formed part of the rigid "skeleton" which is the reason for the low catalytic activity per unit surface of such catalysts in hydrogenation, which was examined in detail in [2].

In examining the pore structure of the samples investigated it should be noted that regardless of the S : W ratio in the WS_2 catalyst, pores with an effective radius of $\sim 13-20$ A predominated. In actual fact, Figs. 1-3 and also 4 show that it is precisely in this radius range that there is a sharp rise on the characteristic curves of A = $f(r_{eff})$ of all the samples studied. Moreover, all the samples studied had a clearly expressed uniform pore structure. A more detailed examination of the data obtained together with the pore structure of sample 3 studied previously in [3] shows that there are more fine and ultrafine pores in samples 1 and 3 than in samples 4 and 5. Thus, the most probable effective pore radius is

somewhat lower in sample 3 (see Figs. 5 and 6 in [3]) and if we compare the values of the specific surface and pore volume of samples 1_{400}, 3_{400}, 4_{400}, and 5_{400} and calculate their mean radii (from the formula $r_{mean} = 2 V/S$), then they are found to equal 17, 17, 24, and 19A, respectively. The somewhat higher specific surface of samples 1_{400} and 3_{400} is evidently caused by their fine pore structure. Thus, as the samples examined were obtained by decomposition of different batches of $(NH_4)_2WS_4$ (at 400° in a stream of H_2), this preparation method always gives uniform fine-pored WS_2 catalysts with a specific surface of 50-65 m^2/g and a pore volume of ~0.05 cc/g regardless of the degree of sulfurization.
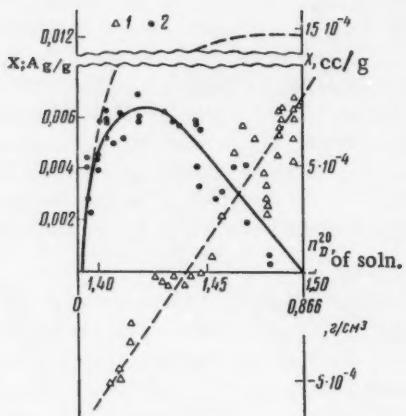
Fig. 6. Isotherms of the adsorption (X) of toluene from a solution in isooctane at room temperature on used WS_2 catalyst 12: 1) First experiment for which the value of X was calculated conditionally; 2) subsequent experiments (sample 13_{400} after pumping out at 400°). The total toluene content in the adsorption volume (A) is shown by a broken line.

Fig. 7. Application of BET equation to isotherms of benzene adsorption at 20° on outgassed WS_2 catalysts obtained by the dynamic method (the scales for the different samples are shown on the ordinate axis): 1) Sample 1_{400}; 2) 9_{20}.

During destructive hydrogenation, coking products are deposited in pores of WS_2 catalysts of all radii. In actual fact, for the pumped out, used samples 10_{400}, 12_{400}, and 14_{400} the characteristic curves have a flatter rise over the whole range of radii (see Figs. 1-3) and, as Fig. 4 shows for samples 4_{400} and 14_{400}, over the whole range of effective radii the pore volume distribution curve of used samples lies below that for unused samples. As the deposition of high-molecular compounds leads to a decrease in pore radius, the most probable effective pore radius of coked catalysts is somewhat less than that of unused catalysts. At the same time, the pore volume distribution with respect to effective radius becomes more uniform as a result of filling of the fine pores with coke and the mean pore radius of coked catalysts (according to the formula $r_{mean} = 2 V/S$) increases as the content of carbonaceous products increases. Thus, for samples 10_{400}, 12_{400}, and 14_{400} r_{mean} equals 20.8, 21.3, and 29.4 A respectively.

As was to be expected, coking leads to a decrease in the pore volume and specific surface of used sample, which is symbatic with the increase in the content of high-molecular products in the catalysts as is shown by the increase in carbon (up to 4.4%) and hydrogen contents (see table).* The inner part of the catalyst tablets was coked much less than layers close to the surface (see table: samples 14, 15, and 16) and as a result the pore volume and specific surface inside the tablet was appreciably greater (see Fig. 1: pumped out samples 14_{400} and 15_{400}) and the mean pore radius appreciably less (22.2 A) than the mean values for the whole catalyst tablet. Data on the chemical composition of samples 14, 15, and 16 given in the table also show that while desulfurization of the WS_2 catalyst occurs during destructive hydrogenation, the middle of the tablet loses somewhat less sulfur.

* The presence of a small amount of carbon in the unused samples was caused by the use of graphite lubricant in the tableting of the WS_2 catalyst.

It should be noted that as is shown by the carbon and hydrogen contents of samples 10, 12, 10_{400}, and 12_{400}, the high-molecular coking products are not removed from the catalyst pores during thermal treatment in vacuum (see table).[*] At the same time, solvents extract some of the coking products from the catalyst even at room temperature. This is shown by the decrease in the carbon content of sample 12 during the preparation of sample 13_{400} from it by treatment with benzene as pumping out at 400° did not affect the carbon content and also by the increase in pore volume and specific surface of sample 13_{400} in comparison with sample 12_{400} (see table and Fig. 2). In accordance with the above, the mean pore radius of sample 13_{400} (19.5 A) was somewhat less than that of sample 12_{400}.

The results of determining the adsorption of benzene and toluene by the samples studied indicate in the first instance that although a WS_2 catalyst is finely porous and contains ultrafine pores with effective radii of less than 10 A, as was established by the adsorption of N_2 [3], practically all the pores of the WS_2 catalyst accessible to nitrogen molecules are also accessible to the larger benzene and toluene molecules. In actual fact, for samples 1_{400} and 13_{400} with cleaned pores, the specific surfaces determined from the adsorption of nitrogen, benzene, and toluene agree well[**] (see table). This conclusion is also confirmed by the quite good agreement between the specific surfaces and pore volumes of sample 3 determined by two different methods: on nitrogen after pumping out at 400° (sample 3_{400}, S = 66 m^2/g and V = 0.057 cc/g [1]) and on benzene after the catalyst pores had been freed from sulfur by treatment with benzene with subsequent pumping out at 20° (see table, sample 9_{20}). Analogous data on the pore structure of a WS_2 catalyst were also obtained from the adsorption of benzene on it by the vacuum-gravimetric method [10].

It should be noted here that the high values for the specific surface found from the adsorption of toluene for samples with filled pores, 1, 3, and 10_{400}, not only do not contradict this conclusion, but confirm some conclusions draw above from data on the adsorption of nitrogen. It is evident that the solution of toluene in isooctane extracted the excess sulfur from the pores of catalysts 1 and 3, as occurred during the treatment of sample 3 with benzene for the preparation of sample 9_{20}. The specific surface of unpumped-out sample 3 from the adsorption of toluene was therefore appreciably higher than from the adsorption of nitrogen (~3 m^2/g [3]). The specific surface of the coked sample 10_{400} given in the table was determined from the adsorption of toluene in the second and subsequent experiments, i.e., after the extraction of high-molecular compounds from catalyst 10 by the toluene–isooctane solution in the first experiment. Since, as was shown above, the coking products were not removed from the pores of a WS_2 catalyst by thermal treatment in vacuum, the specific surface of pumped-out sample 10_{400} determined from the adsorption of nitrogen was less than the value determined from the adsorption of toluene in the second and subsequent experiments. Thus, these data confirm the above conclusions that solvents extract sulfur and some of the high-molecular coking products from the pores of a WS_2 catalyst. It should also be noted that a comparison of the specific surfaces of the unpumped-out sample 1 and the pumped-out sample 1_{400}, determined from the adsorption of toluene, provides further confirmation for the liberation of excess sulfur from the pores of a WS_2 catalyst during its thermal treatment.

Part of the work was carried out in the catalyst research laboratory of the N. D. Zelinskii Institute of Organic Chemistry and the author is very grateful to A. M. Rubinshtein for valuable advice.

SUMMARY

1. A study was made of the pore structure of WS_2 catalysts with various atomic ratios of S : W, both unused and used in industrial destructive hydrogenation.

2. The pore structure of an unused catalyst was independent of the S : W ratio and its pores which were accessible to nitrogen molecules were also accessible to the larger molecules of benzene or toluene.

3. The pores of an unused catalyst with S : W < 2 were filled with sulfur or compounds of it.

4. Coke was deposited in the catalyst pores of all radii during destructive hydrogenation at ~400°.

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[*] The presence of a small amount of carbon in the unused samples was caused by the use of a graphite lubricant in the tableting of the WS_2 catalyst.

[**] To study the changes in the pore structure of a WS_2 catalyst during its cooking, it is therefore possible to use data on the pore structure of samples pumped out after use, as was done in the present work.

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All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. *Some or all of this periodical literature may well be available in English translation.* A complete list of the cover-to-cover English translations appears at the back of this issue.

ISOTOPE EXCHANGE STUDY OF THE ELECTROPHILIC
REPLACEMENT REACTION IN A SATURATED CARBON ATOM
COMMUNICATION 3. ISOTOPE EXCHANGE IN ESTERS OF α-
BROMMERCURYARYLACETIC ACIDS WITH MERCURIC BROMIDE,
LABELED WITH Hg^{208}, IN AQUEOUS DIOXANE

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It was shown in a previous communication [1] that the isotope exchange reaction of the ethyl ester of α-brommercury phenylacetic acid with $HgBr_2$ in aqueous dioxane follows a first order kinetic equation, and a mechanism was proposed involving preliminary ionization of the mercurio-organic compound

$$C_6H_5-CH-COOC_2H_5 \rightleftarrows C_6H_5-\overset{\ominus}{CH}-COOC_2H_5 \qquad (1)$$
$$| \qquad\qquad\qquad\qquad \overset{\oplus}{HgBr}$$
$$HgBr$$

$$C_6H_5-\overset{\ominus}{CH}-COOC_2H_5 \quad \rightarrow C_6H_5-\overset{\ominus}{CH}-COOC_2H_5+HgBr_2 \qquad (2)$$
$$\overset{\oplus}{HgBr} \quad +Hg^*Br_2 \leftarrow \overset{}{\oplus Hg^*Br}$$
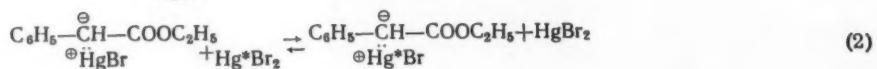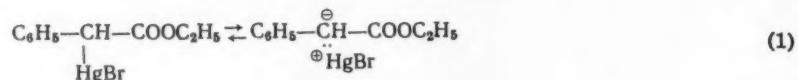
The present paper presents data on the study of the effect of structural factors (principally polar) on the reaction rate.

EXPERIMENTAL

The compounds chosen for study were the ethyl esters of mercurated substituted phenylacetic acids $XC_6H_4CH(HgBr)COOC_2H_5$, were X = p-F, Cl, Br, I, CH_3, t-C_4H_9 and o-CH_3.
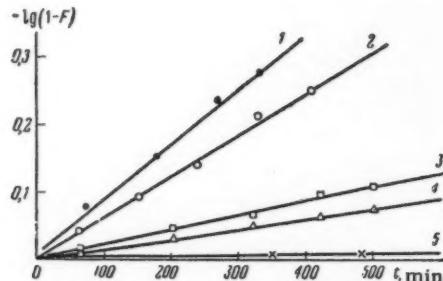
Log (1-F) as a function of $\underline{t}$ for the isotope exchange of $XC_6H_4CH(HgBr)COOC_2H_5$ with Hg^*Br_2 and aqueous dioxane at 60° X: 1) p-Br; 2) p-F; 3) o-CH_3; 4) p-CH_3; 5) p-t-C_4H_9.

The reaction kinetics was studied by the method described previously in [2] in 70% aqueous dioxane at 60°. The data are given in the table. The rate constants were calculated from the half exchange periods found graphically from the Figure. The mean accuracy of determining τ 1/2 did not exceed 10%.

Kinetics of Isotopic Exchange of $XC_6H_4CH(HgBr)COOC_2H_5$ with Hg^*Br_2 and 70% Aqueous Dioxane at 60°

X	Time, min	A_{HgBr_2}, counts/min	$A_{Hg\text{-}ester}$ counts/min	F, %	$\tau_{1/2}$, min	$K_1 \cdot 10^4$, min^{-1}
H c=0,02 *	100	1021	61	11,2	620	5,58
		1190	72	11,4		
	200	1118	107	17,5		
		1131	130	20,6		
	300	905	152	28,8		
		1093	166	26,4		
	400	956	205	35,4		
		1017	231	37,1		
	430	755	240	48,3		
		941	252	42,2		
H c=0,04	100	1847	117	11,9	620	5,58
		1686	112	12,4		
	200	1873	259	24,2		
		1659	225	23,9		
	300	2110	361	29,2		
		2228	346	26,9		
	400	1622	372	37,3		
		1957	419	35,4		
p-F	60	1048	69	12,4	480	6,93
		1209	58	9,2		
	150	1000	103	18,7		
		1063	107	18,3		
	240	1035	167	27,8		
		1155	197	29,1		
	330	987	222	36,8		
		850	214	40,2		
	410	1057	299	44,1		
		1145	317	43,4		
p-F	70	1244	58	8,9	520	6,93 **
	180	1189	118	18,1		
	270	1234	214	29,6		
	330	995	181	34,8		
p-Cl	60	808	57	13,2	330	10,5
		878	60	12,8		
	150	952	146	26,6		
		1009	146	25,4		
	240	904	221	39,3		
		896	192	35,3		
	330	855	309	53,0		
		709	245	51,3		
	410	975	353	53,2		
		835	343	58,2		
p-Br	70	1082	92	15,7	360	9,63
	180	1264	216	29,2		
	270	1090	281	41,0		
	330	1382	422	46,7		
p-J	60	1708	51	13,5	340	10,2
		805	53	12,4		
	150	969	145	26,0		
		1092	175	27,7		
	240	830	225	42,7		
		1337	286	35,2		

X	Time, min.	A_{HgBr_2}, counts/min	$A_{Hg\text{-}ethers}$, counts/min	F, %	$\tau_{1/2}$, min	$K_1 \cdot 10^4$, min^{-1}
	330	947	276	45,2		
		751	218	45,0		
	410	923	371	57,3		
		715	277	55,9		
	60	1904	34	3,5		
	200	1359	73	10,2		
		1207	72	11,2		
o-CH$_3$	320	1732	137	14,6	1370	2,30
		1399	100	13,3		
	420	1251	136	19,6		
		995	108	19,6		
	500	1568	185	21,1		
		1627	194	21,3		
	60	1376	20	2,9		
		1744	25	2,8		
	200	1421	56	7,6		
		1524	49	6,2		
p-CH$_3$	320	1548	108	13,0	1900	1,80
		1585	79	9,5		
	420	1365	102	14,0		
	500	2396	210	16,1		
		2058	183	16,3		
	150	1095	21	3,8		
		1078	18	3,3		
p-t-C$_4$H$_9$	350	908	27	5,8	3000	1,20
		1277	60	8,7		
	480	1508	94	11,7		
		1490	76	9,7		

* In all cases, unless specially noted, the concentration of each reagent is equal to 0.03 mols/liters, A_{HgBr_2} is the activity of the mercuric bromide $Z_{Hg\text{-}ester}$ is the activity of the mercuro organic compound.
** The constant is the mean of the results of two experiments with $FC_6H_4CH(HgX)COOC_2H_5$.

It is clear from the results of the measurements that electron donor substituents considerably slow down the reaction, while electron acceptors (halogens) accelerate it considerably. There is no difference between the effect of chlorine, bromine and iodine as is the case in some other reactions [3, 4]. The effects shown by alkyl groups is particularly large. Thus introducing a methyl group into the benzene ring in the para position slows down the reaction threefold, and tertiary butyl slows it down fivefold. An effect of this sort from electron donor and electron repulsive groups is in agreement with the mechanism which we proposed for the exchange under study. Gammet's equation was not found to be applicable to the series of data obtained.

SUMMARY

A study of the isotope exchange of the ethyl esters of α-brommercuryarylacetic acids with [203]Hg Br$_2$ and 70% aqueous dioxane at 60°, made it possible to arrange the substituents in the following series in order of decreasing reaction rate: p-I, Br, Cl > p-F > H > o-CH$_3$ > p-CH$_3$ > p-typet. C$_4$H$_9$.

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THE INFLUENCE OF γ-RADIATION ON THE ACTIVITY
OF CATALYSTS CONTAINING PLATINUM

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In our preceeding work [1] on the investigation of the action of radiation (0.6 Mev γ) on the catalytic activity for the decomposition of hydrogen peroxide of aluminum silicate containing 0.5% platinum it was shown that after irradiation in a nitrogen atmosphere there occurred an increase in the activity of the catalyst; this consequence of the radiation was of long duration. In the present work our problem was to investigate the influence of γ-radiation on the catalytic activity of catalysts containing platinum when the irradiation was conducted in air. The subject of our investigation was platinum-black: two samples of 1% Pt on Al_2O_3 (samples A and B), and one of 10% Pt on Al_2O_3.

EXPERIMENTAL

The platinum-black was obtained by the reduction of chloroplotinic acid with 30% formaldehyde in a basic medium. For each gram of platinum-black we used 3 ml of a 30% aqueous solution of formaldehyde and 5 ml of 50% potassium hydroxide. After washing the platinum-black until a negative reaction for Cl^- was obtained in the wash water, the catalyst was transferred to the catalytic tube where it was dried in a stream of hydrogen and was thereafter reduced at 330° for 8 hours. The aluminum oxide was prepared in the following manner. Hydrated aluminum oxide was precipitated from a 1 M solution of aluminum nitrate by 12% aqueous ammonia. The hydro-gel was washed free of NO_3^- ion, and was filtered off and dried at 130-140° for 6-8 hrs. The product was heated to 500° for 3 hrs. The 1% Pt/Al_2O_3 (samples A and B) and 10% Pt/Al_2O_3 catalysts were prepared by adding the calculated quantity of chloroplatinic acid solution to the aluminum oxide with subsequent dehydration at 120-130° for 4 hrs. The 1% Pt/Al_2O_3 (sample A) and 10% Pt/Al_2O_3 catalysts were reduced in a stream of electrolytic hydrogen at 330° for 8 hrs before use, but catalyst sample B was heated to a temperature of 1000-1050° for 10 hrs. The catalysts were then sealed into glass ampoules (5 ampoules of each catalyst); part of these were irradiated, the remainder were kept for subsequent comparison of catalytic activity.
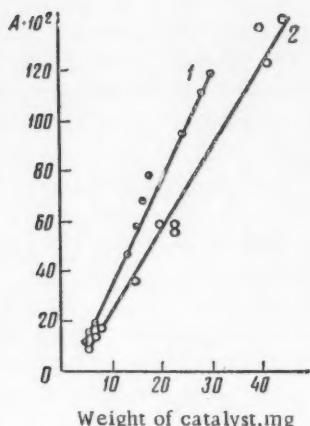
Fig. 1. The influence of γ-radiation on the activity of platinum-black: 1) Unirradiated catalyst; 2) irradiated catalyst.

The determination of the catalytic activity of the catalysts, both those subjected to radiation and the unirradiated samples, were carried out 7 months after their preparation and 7 days after the irradiation. The irradiations were made with 0.6 Mev γ-rays. The irradiation dose in all cases was $60 \cdot 10^{19}$ V/r. The activities of the catalysts were determined for the decomposition of 8 ml of a 5.30% solution of hydrogen peroxide. The reaction was carried out in a thermostated glass shaker. The rate of mixing in all cases was 500 shakes/min. All the experiments were carried out at 25 ± 0.05°. The rate of the reaction was measured by the evolution of oxygen. The volume of oxygen evolved as a result of the reaction was recorded by an automatic gasometer constructed for precision work in the electromechanical shop of our Institute by I. A. Lavrov. A test of the apparatus showed that automatic recording considerably increased the sensitivity of the experiments. The gasometer measured the volume of gas at a set pressure (760 ± 10 mm Hg); this was maintained under the conditions of our experiment with a sensitivity of ± 0.01 mm of mercury. As a measure of the catalytic activity we provisionally took the value inversely proportional to the time of half-decomposition $A = 1/\tau$ of the

initial quantity of hydrogen peroxide. The dependence of A on the size of the aliquot was investigated for each sample. Conclusions on the influence of γ-radiation on the activity of the catalysts investigated were drawn from a comparison of these curves. The data obtained are given in Figs. 1-4.
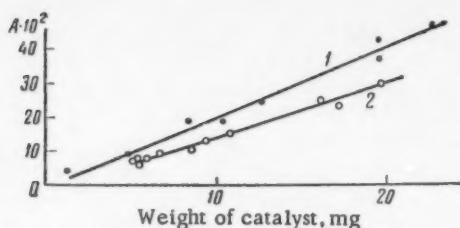
Fig. 2. The influence of radiation on the catalytic activity of 10% Pt/Al$_2$O$_3$: 1) Unirradiated catalyst; 2) irradiated catalyst.
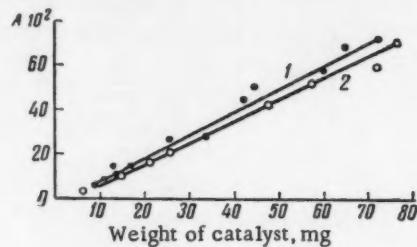
Fig. 3. The influence of radiation on the catalytic activity of 1% Pt/Al$_2$O$_3$ (sample B): 1) Unirradiated catalyst; 2) irradiated catalyst.

In Fig. 1 are given the dependences between and the size of the aliquots of platinum-black—irradiated and non-irradiated. As is clear from the Figure, the curve for the irradiated catalyst lies considerably lower than the curve for the unirradiated sample; i.e., a deactivation of the platinum-black has occurred following irradiation. Similar curves for 10% Pt/Al$_2$O$_3$ given in Fig. 2 also definitely show deactivation of the catalyst by the action of γ-radiation. Sample A of the 1% Pt/Al$_2$O$_3$ (Fig. 3) showed only a very slight decrease of catalytic activity following irradiation, and for sample B of the 1% Pt/Al$_2$O$_3$ there was no observable change of catalytic activity due to irradiation (see Fig. 4).

From the data cited above it follows that the deactivating effect of irradiation in air is augmented by an increase in the quantity of platinum in the catalyst. Thus, the catalytic activity of platinum-black itself fell by 32% following irradiation, while in the case of aluminum oxide containing 10% platinum a deactivation of 20% occurred, and for 1% Pt/Al$_2$O$_3$ (sample A) only an insignificant change of the catalytic activity was observed, approximately 7%. Sample B of the 1% Pt/Al$_2$O$_3$ showed no change of catalytic activity whatever after irradiation.
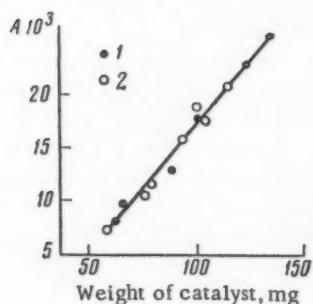
Fig. 4. Absence of the effect of irradiation on the catalytic activity of 1% Pt/Al$_2$O$_3$ (sample B): 1) Catalyst unirradiated; 2) Catalyst irradiated.

It is reported in the literature [2, 3] that there is a diminution of the catalytic activity of catalysts kept in air. The nature of this phenomenon has not been completely explained. It is possible that it is connected with a recrystallization which is accelerated in the presence of oxygen. One can propose that in the presence of "hot" oxygen atoms excited by irradiation [4] this process of deactivation proceeds faster. The fact that adsorbed catalysts are less subject to deactivation than platinum-black itself may be connected with the increased difficulty with which structural change can take place in the metal in the presence of the carrier.

Our supposition finds some confirmation in the results of the investigation of the 1% Pt/Al$_2$O$_3$ catalysts (samples A and B). In the case of the catalyst obtained by reduction in the soft condition (sample A) a change in the activity of the catalyst after irradiation was observable, while the 1% Pt/Al$_2$O$_3$ (sample B) obtained by the thermal decomposition of H$_2$PtCl$_6$ at high temperature, and therefore recrystallized to a greater extent, showed no observable change of activity after irradiation.

SUMMARY

1. The action of a dose of 60 · 10^{19} V/r of 0.6 Mev γ-radiation on the catalytic activity of catalysts containing platinum was investigated for the decomposition of hydrogen peroxide.

2. Radiation caused a deactivating effect, which increased with an increase in the quantity of platinum in the catalysts investigated.

3. The 1% Pt/Al$_2$O$_3$ catalyst obtained by the thermal decomposition of adsorbed H$_2$PtCl$_6$ did not show a change of catalytic activity after irradiation.

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AN INVESTIGATION OF THE CHEMICAL CONDITION
OF RADIOPHOSPHORUS IN CRYSTALS OF POTASSIUM
CHLORIDE IRRADIATED WITH HIGH-ENERGY PROTONS

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The condition of oxidation of the radiophosphorus which is formed by the Cl^{35} (n, α) P^{32} reaction when the chlorides of the alkali metals are irradiated with fast neutrons has been studied by a number of investigators [1-4]. However the character of the change of the chemical condition of the P^{32} in the processes of thermo- and radiation-induced annealing has not been investigated. The position of the P^{32} in the crystal lattice has also remained on open question, as has its interaction with the ions proper to the lattice itself. The present communication reports on part of an investigation devoted to the study of the existing forms and the chemical transformations of the radiophosphorus in the alkali halide system [5, 6]. In order to obtain radiophosphorus in crystals of potassium chloride the latter was bombarded with high-energy protons. The radiophosphorus arose from the reactions of deep spallation.

$$Cl_{17} (p;\ 3p,\ xn)\ P^{32}_{15} \text{ и } K_{19} (p;\ 5p,\ xn)\ P^{32}_{15}$$
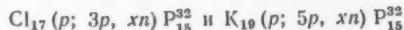
EXPERIMENTAL

Single crystals of potassium chloride, grown in air according to the method of Kyropoulus from molten, chemically pure potassium chloride were used as the targets. The samples ($0.2 \cdot 1.2 \cdot 1.2$ cm) were heated at a temperature of 650-700° for 6 hrs in an atmosphere of purified nitrogen, and then were slowly cooled to room temperature. The crystals thus prepared were irradiated with an external stream of 660 Mev protons. The total current during the time of irradiation was 10^{12}-10^{13} protons per square centimeter of the target. The radiophosphorus, which was usually isolated in the experimental series as magnesium ammonium phosphate, possessed satisfactory radiochemical purity. For the study of the kinetics of the thermal annealing of the irradiated crystals they were heated in an electric furnace the temperature of which could be maintained with a sensitivity of $\pm 2°$.

The active chloride crystals were dissolved in water which contained the following ions as carriers: PO_4''', HPO_3'' and H_2PO_2'; the phosphate ions were separated as magnesium ammonium phosphate [7]. The phosphite was oxidized with iodide in a medium containing ammonium borate to the phosphate [8, 9], and was precipitated with a magnesia mixture. The hypophosphite was not noticeably oxidized under these conditions, while the phosphite was oxidized practically completely. Finally, after oxidation with bromine to the phosphate, the hypophosphite was precipitated. The percent composition of each of these forms was found as the ratio of the activity of the given fraction to the total activity of the phosphorus in the three forms, which was taken to be 100%. It was observed that crystals of potassium chloride which were subjected to a high temperature annealing before irradiation contained 10-20% of the P^{32} activity in the phosphate fraction, while for crystals which were not treated in this manner the part in this fraction rose to 50-60%. The initial distribution of the radiophosphorus in the annealed crystals somewhat differed in the two experimental series (Table 1). As is clear from the curves of Figs. 1-4, the oxidation of the radiophosphorus proceeds rapidly in the beginning, but much more slowly in the second stage. In all cases there occurs a decrease of the quantity of radiophosphorus in the hypophosphite fraction, and, at its expense, an increase of the quantity of radiophosphorus in the two other valence forms. During the fast stage of the oxidation there is a characteristic simultaneous growth of the phosphate and phosphite fractions. At 200° the rate of the oxidation continuously decreases, and after about 8 hrs of annealing, the curves practically form "plateaus." While at this temperature the transformation $HP^{32}O_3'' \rightarrow P^{32}O_4'''$ is not observed, at a higher temperature, as is clear from Figs. 2, 3, and 4, the quantity of radiophosphorus in the phosphite fraction reaches a maximum at a particular moment of the annealing process, and on further heating it decreases, increasing the phosphate fraction.
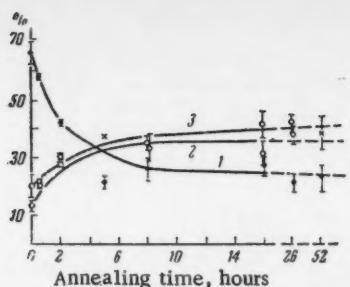
Fig. 1. The change of the content of the valence forms of radiophosphorus in KCl crystals during the annealing process at 200°: 1) $H_2P^{32}O_2'$; 2) $HP^{32}O_3''$; 3) $P^{32}O_4'''$.
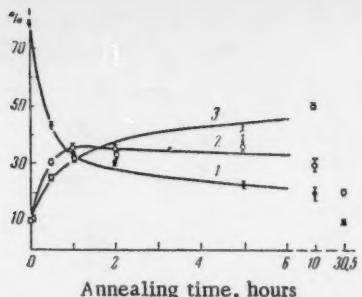
Fig. 2. The change of the content of the valence forms of radiophosphorus in KCl crystals during the process of annealing at 250°: 1) $H_2P^{32}O_2'$; 2) $HP^{32}O_3''$; 3) $P^{32}O_4'''$.
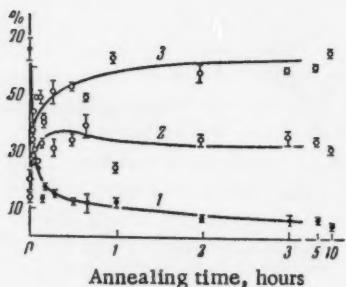
Fig. 3. The change of the content of the valence forms of radiophosphorus in KCl crystals during the annealing process at 300°: 1) $H_2P^{32}O_2'$; 2) $HP^{32}O_3''$; 3) $P^{32}O_4'''$.
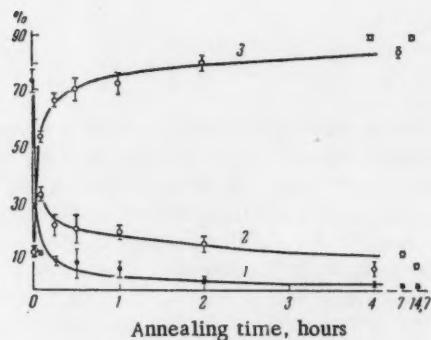
Fig. 4. The change in the content of the valence forms of radiophosphorus in KCl crystals during the annealing process at 400°: 1) $H_2P^{32}O_2'$; 2) $HP^{32}O_3''$; 3) $P^{32}O_4'''$.

It was interesting in this investigation of the oxidation condition of radiophosphorus to consider phosphine in addition to the oxidized forms of the radiophosphorus. For this purpose, a solution which contained phosphate, phosphite, and hypophosphite ions was saturated with phosphine before dissolution of the crystals; after dissolution of the crystals, the phosphine was removed from the solution with a current of nitrogen gas, and was absorbed in a vessel containing bromine water. The isolation of the individual oxidized valence forms was then carried out as before. Some preliminary results of the study of the initial distribution are given in Table 2. A considerable scatter in the yields of the $H_2P^{32}O_2'$ and $P^{32}H_3$ fractions was observed which to some extent can be ascribed to the incompleteness of the method. The kinetics of the transformation of the phosphine fraction have not been fully studied, but some experiments have shown that the activity in the phosphine fraction disappears earlier than in the hypophosphite fraction. Several experiments carried out for the purpose of observing atomic radiophosphorus in the irradiated crystals gave negative results. The experiments were based on the methods described in the work of Carlson and Coski [3].

DISCUSSION OF THE EXPERIMENTAL RESULTS

Recoil atoms such as P^{32} transfer their energy at the ends of their paths to a very small volume of the crystal, and thus become localized inside a region of the crystal which has been subjected to strong radiation disruption, and which contains a large number of defects which have not been able to recombine during the time of the existence of the "displacement spike" [10-12]. If it is considered that the multiply charged ions have succeeded in recombining, then taking into consideration the first ionization potentials of the Cl, P and K atoms and also the accidental position of the phosphorus atom, as a working hypothesis the lower oxidized states of the radiophosphorus (−1, 0, +1) can be taken as more probable.

TABLE 1. The Initial Distribution of Radiophosphorus in KCl as the Fractions: Phosphate, Phosphite and Hypophosphite

Isotherms	Distribution of phosphorus, %			No. of experiments
	$P^{32}O_4'''$	$HP^{32}O_3''$	$H_2P^{32}O_2'$	
200 and 300°	19.9 ± 4.1	13.5 ± 1.8	66.6 ± 4.6	12
250 and 400°	11.8 ± 2.2	12.5 ± 1.9	75.7 ± 3.5	40

TABLE 2. The Initial Distribution of Radiophosphorus in KCl in the Fractions: Phosphate, Phosphite, Hypophosphite and Phosphine (average of six experiments)

$P^{32}O_4'''$	Distribution of phosphorus, %		
	$HP^{32}O_3''$	$H_2P^{32}O_2'$	$P^{32}H_3$
13±1	12±2	43±7	32±10

During the rapid stage of the thermal annealing of the irradiated crystals, the principal occurrences are electron transfers between atoms and ions, restoring the close order in the lattice; a considerable part of the defects of the lattice recombine. The radiophosphorus, interacting with the mobile atoms of chlorine which have arisen as a result of the radiolysis, increases its positive charge and occupies cationic positions in the lattice. However the further increase of the positive charge requires the presence of cationic vacancies around the phosphorus ion in order to compensate for its excess charge and thus to maintain the condition of electrical neutrality. In this case, the pentavalent phosphorus would have to enter into the composition of a negative complex* of the type $[P^{5+}4K\,\square\,6Cl^-]^-$, where $K\,\square$ is a vacant site of a potassium ion. One might suggest that the diffusion of the cationic vacancies to the atoms of radiophosphorus could become the determining process in the kinetics of the slow stage of the oxidation.

It is difficult to say if the oxygen dissolved in the potassium chloride lattice plays any kind of role in the oxidation of the radiophosphorus. It is ordinarily considered that crystals grown in air from the melt contain hydroxyl ions. The increased content of the higher oxidized states of the radiophosphorus in unannealed crystals can be explained by the presence in the lattice of oxygen and of defects of a biographic character: dislocations, internal surfaces, etc., since these could appear as electron traps. However it is improbable that in degassed and annealed crystals during the rapid stage of the process of oxidation oxygen plays a greater role than the atomic chlorine formed by the radiolysis. The oxygen compounds of phosphorus isolated by us are more probably formed in the solution than in the crystal. Although they appear as products of the hydrolysis of the chemical forms which are produced in the crystal, there is no basis for considering that the general picture of the chemical transformations of the radiophosphorus which we have disclosed are strongly distorted by secondary processes occuring in solution. The negative results of the analyses for atomic phosphorus, however, do not exclude its presence in the crystal. According to the note of Coski [3], atomic phosphorus can enter into an exchange with its carriers which proceeds more slowly than the possible reaction with the molecules of water which are more often encountered.

Another fact which could be explained by secondary processes occurring during the solution of the crystal is the parallel growth of the phosphate and phosphite fractions observed by us during the rapid stage of the oxidation process. It could be suggested that the formation of $HP^{32}O_3''$ and $P^{32}O_4'''$ occurs through the interaction of the intermediate form PCl_4 with water; this would with equal probability be oxidized and reduced in water with the formation, respectively, of PO_4''' and HPO_3''. Besides this, this form is gradually oxidized in the crystal to PCl_5. Of course, the existence of quadrivalent phosphorus is debatable even in such an unusual medium as the irradiated crystal.

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* A negative effective charge was determined by us in a study of the electrolytic migration of radiophosphorus in KCl crystals [5].

In this way, starting from the experimental data it would be possible to crudely represent the sequential reactions of the oxidation of radiophosphorus which occur in the crystal by two hypothetical schemes:

$$P(-1,0+1 \text{ ext. })\Big\langle \begin{matrix} \nearrow K_3PCl_6 \\ | \\ \searrow KPCl_6 \end{matrix} \quad \text{or} \quad P(-1,0+1 \text{ etc. })\Big\langle \begin{matrix} \nearrow K_2PC \\ | \\ \searrow KPCl_6 \end{matrix}$$
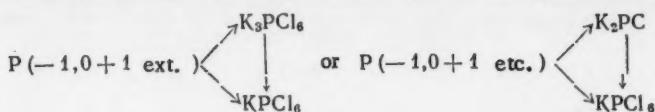
The octahedral configurations of $PCl_6^{-(6-z)}$, where $\underline{z}$ is the charge on the phosphorus ion, are formed when the radiophosphorus occupies a cationic site in the lattice. If it is found interstitially, then it is surrounded by four chloride ions, and together with them forms the tetrahedral ion $PCl_4^{-(4-z)}$.

As analysis shows, the isothermal curves (Figs. 1-4) do not follow the kinetics of first order reactions. In all probability the transformations observed by us are diffusion controlled with a changing number of agents (cationic and anionic vacancies, atoms of chlorine) responsible for the kinetics of the oxidation of the radiophosphorus. After obtaining a large number of isotherms, and also after doing research with the use of phosphine as a carrier, attempts will be made to examine the experimental curves on the basis of representations of the processes taking place with consideration of their activation energies [13].

SUMMARY

1. The lower valence conditions of radiophosphorus predominate in crystals of potassium chloride irradiated with 660 Mev protons for a total current of approximately 10^{12}-10^{13} protons/cm^2.

2. The oxidation of the radiophosphorus atoms during the isothermal annealing of the irradiated crystals proceeds in several steps and has the character of sequential reactions.

3. It is necessary to consider the chemical transformations of the radiophosphorus in the irradiated crystals as reactions of the radiophosphorus with the products of radiolysis and with the centers of disruption produced by the irradiation.

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COMBINATION DISPERSION [RAMAN] SPECTRA
OF CERTAIN BENZENE-SERIES HYDROCARBONS
WITH ONE OR TWO SIDE CHAINS

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In work published previously [1] an attempt was made to extend the combination [Raman] method of analysis of gasolines [2] to the aromatic portion of ligroin boiling above 150°. In view of the absence of an adequate number of standard spectra, we were obliged to forego the determination of the individual hydrocarbon composition of the fractions boiling above 175-180° and, in a number of cases, to limit ourselves to establishing the narrow group composition. Such groups include hydrocarbons with an identical type of substituent on the benzene ring, characteristic lines being distinguished for the spectra of each group, sufficiently close in frequency and without any sharp difference in intensity. Based on the available data, spectral criteria were established for the following groups: monoalkylbenzenes, 1,2- and 1,3-dialkyl benzenes, 1,2,3-, 1,2,4- and 1,3,5-trialkylbenzenes, and certain more complex aromatic compounds.

Unfortunately, the frequencies and intensities of the characteristic lines in a number of cases were derived from a small number of spectra. Moreover, of necessity, use was also made of literature data obtained under different and not always comparable conditions. Thus, the authors of a number of works were limited to measuring the position of the lines and only a visual estimation of their intensity. On the other hand, the data cited in the well-known works of American investigators who used a photographic method of recording [3] are insufficiently accurate, as has already been noted [4]. However, since the photographic method has been used to measure a considerable number of analytically important spectra of difficultly available hydrocarbons, an attempt was made to recalculate their intensities to the scale which we adopted [5], even though these results also did not turn out to be very reliable. Nevertheless, recalculated data, in the absence of others, are utilized widely. Hence it is clear that new, more accurate measurements of the frequencies and intensities under the conditions recommended for the combination [Raman] method of analysis of gasolines [2] are extremely desirable.

EXPERIMENTAL

In the present work, results are shown for an investigation of the Raman spectra of certain benzene-series hydrocarbons with one or two side chains. All of the hydrocarbons utilized in the present work were obtained in very pure form. The spectra of the isobutylbenzenes, 1-methyl-4^2-method-4-butylbenzene, and 1,4-di-tert-butyl benzene were studied for the first time; the other spectra had already been encountered in the literature. The method of obtaining the spectra and their measurements were described previously [6]. For each hydrocarbon the preparative method is described briefly and the basic constants are given, along with the most reliable literature data for comparison.

Isobutylbenzene. Obtained by hydrogenating a mixture of 2-methyl-3-phenylpropene-1 and 2-methyl-1-phenylpropene-1 (see below) at atmospheric pressure and room temperature in the presence of palladinized carbon, activated with palladium chloride. The resulting compound was purified by vacuum distillation in a 100-theoretical-plate column [7]. Properties: b.p. 113.3° (132 mm); n_D^{20} 1.4865; d_4^{20} 0.8532. Literature data [8]: b.p. 172.759° (760 mm); n_D^{20} 1.48646; d_4^{20} 0.85321.

$\Delta \nu$ (cm^{-1}): 210 (3, sh. f); 251 (39, sh); 308 (32); 399 (2); 425 (12); 452 (1); 486 (4); 497 (20); 595 (7); 622 (44); 739 (37); 786 (4); 807 (15); 816 (38); 825 (8, f); 842 (6); 856 (2); 880 (5); 892 (3); 924 (5); 948 (33); 958 (20); 991 (4); 1004 (280); 1031 (78); 1058 (8, sh); 1081 (3, sh); 1100 (5, sh); 1119 (32); 1157 (26); 1179 (21); 1206 (64); 1222 (8, sh); 1284 (23); 1326 (14); 1343 (22, sh); 1446 (31); 1461 (27); 1498 (1); 1527 (2); 1584 (25); 1596 (10, f); 1606 (74); 2711 (10); 2761 (20, sh); 2849 (60); 2867 (160, r); 2885 (90, sh. f); 2916 (130, sh. f); 2932 (100, sh. f); 2956 (140); 2966 (140); 2981 (30, sh. f); 3033 (100); 3054 (180, r); 3065 (160).

tert-Butylbenzene. Obtained by alkylation of benzene with tert-butyl alcohol in the presence of aluminum chloride and purified by chromatography on silica gel, and then by vacuum distillation in a 100-theoretical-plate column. Properties: b.p. 75.5° (33.5 mm); n_D^{20} 1.4927; d_4^{20} 0.8666. Literature data [8]: b.p. 169.119° (760 mm); n_D^{20} 1.49226; d_4^{20} 0.86650.

$\Delta \nu$ (cm^{-1}): 140 (160, sh. f); 208 (2, sh); 237 (2, sh. f); 321 (15, sh); 351 (12, sh); 392 (3, sh); 408 (2, sh); 457(4); 534(41); 548 (3); 593 (2); 622 (42); 678 (3,sh); 707 (155); 740 (2, sh); 765 (11); 786 (3); 808 (2); 839 (24); 931 (35, dr); 990 (10, r); 1003 (300); 1023 (4, sh. f); 1033 (125); 1086 (3); 1115 (58); 1158 (32); 1192 (54); 1205 (54); 1244 (1); 1270 (23); 1289 (3); 1302 (2); 1334 (3); 1445 (44); 1470 (32); 1583 (22); 1604 (70); 2864 (80); 2901 (160); 2927 (100, f); 2967 (230, sh); 3022 (30); 3052 (100, f); 3063 (250); 3162 (20); 3202 (20).

Cyclohexylbenzene. An unpurified preparation of this hydrocarbon, obtained from E. M. Terent'eva, was freed of unsaturates by treatment with Kaufman bromine solution [9] at room temperature. It was further purified, as for the preceding hydrocarbon, by chromatography and distillation, the only difference being that the distillation was conducted in a 60-theoretical-plate column. Properties: b.p. 125.7° (26.5 mm), freezing point (f.p.) 7.2°; n_D^{20} 1.5262; d_4^{20} 0.9426. In the literature there are reliable data only for the freezing point [10]: 7.070°. In view of the contradictory information on the other constants, the values cited here are those set in bold-face type in the well-known book of Egloff [11]: b.p. 238.1° (760 mm); n_D^{20} 1.5249; d_4^{20} 0.9431. It may be considered that our constants are the more reliable.

$\Delta \nu$ (cm^{-1}): 192 (2, sh); 240 (3, sh); 278 (62); 376 (2); 403 (4); 438 (10, sh); 462 (10, sh); 497 (4); 522 (7, sh); 585 (2); 622 (60); 748 (5); 775 (56); 788 (4); 805 (3); 829 (21); 863 (19); 885 (3, sh. f); 894 (9); 923 (5); 977 (10); 996 (170); 1002 (170); 1030 (76); 1048 (41); 1076 (10); 1100 (8); 1131 (16); 1155 (22); 1180 (33); 1200 (62); 1231 (18); 1265 (16); 1281 (13); 1298 (15); 1329 (13); 1348 (8); 1369 (6); 1442 (62); 1463 (6, f); 1582 (22); 1602 (82); 2852 (210); 2882 (80, f); 2919 (180); 2935 (220); 2979 (15, sh. dv); 3002 (30, f); 3033 (60); 3053 (80, sh. f); 3065 (150, sh).

2-Methyl-3-phenylpropene-1. Obtained in mixture with 2-methyl-1-phenylpropene-1 by dehydration (under the action of several drops of concentrated sulfuric acid) of dimethyl benzyl carbinol, prepared by interaction of benzylmagnesium chloride with acetone. 2-Methyl-3-phenylpropene-1 was isolated from the mixture by vacuum distillation in an 80-theoretical-plate column with copper packing. Properties: b.p. 76.3° (27 mm); n_D^{20} 1.5081; d_4^{20} 0.8825. Literature data [12]: b.p. 175.8° (760 mm); f.p. −33.96°; n_D^{20} 1.5083; d_4^{20} 0.8821.

$\Delta \nu$ (cm^{-1}): 174 (15, sh); 240 (30, sh); 265 (5, sh); 310 (25, sh); 336 (3, sh); 356 (3, sh); 382 (7, sh); 412 (10, sh); 454 (8, sh); 495 (29); 600 (19); 621 (52, r); 648 (5); 706 (20); 739 (36); 809 (7, sh. f); 822 (72); 843 (5, sh); 891 (10, sh); 962 (4); 992 (4); 1004 (360, r); 1031 (84, r); 1155 (25); 1176 (41); 1194 (45); 1207 (26); 1230 (1); 1277 (12); 1293 (10); 1335 (12); 1375 (8); 1395 (8); 1420 (37); 1430 (25, f); 1450 (5, sh. f); 1497 (4); 1585 (37); 1603 (62, sh); 1650 (66, sh); 2836 (30, sh); 2897 (90, sh); 2919 (110, sh); 2943 (50, sh); 2985 (90, sh); 3038 (70, f); 3054 (190, r); 3068 (170, r);

2-Methyl-1-phenylpropene-1. Obtained together with the previous compound and isolated by distillation as indicated above. Properties: b.p. 87.9° (27 mm); n_D^{20} 1.5339; d_4^{20} 0.9022. Literature data [12]: b.p. 187.7° (760 mm); f.p. −50.60°; n_D^{20} 1.5406; d_4^{20} 0.9050.

$\Delta \nu$ (cm^{-1}): 228 (12, sh); 278 (20, sh); 331 (30); 352 (5); 407 (36); 430 (82); 467 (66); 512 (90); 619 (54, r); 632 (20); 741 (54); 809 (72); 837 (120, sh. dv); 859 (90, r); 983 (50, sh); 1001 (600, r); 1030 (90, r); 1055 (30); 1072 (34); 1101 (6); 1155 (58, r); 1182 (125); 1223 (380, r); 1249 (3); 1291 (46, r); 1330 (8); 1380 (98); 1439 (140, r); 1455 (130, r); 1493 (62); 1575 (45); 1598 (960, sh); 1658 (1050, sh); 1708 (10, sh); 2856 (80, sh); 2873 (90, sh); 2914 (230); 2933 (140, sh); 2972 (70); 3028 (30); 3049 (160, f); 3065 (230).

1-Methyl-4-isopropylbenzene (p-Cymene). Isolated from a technical sample, freed of unsaturates by treatment with Kaufman bromine solution [9] at room temperature. Then the vacuum-distilled preparation was chromatographed on silica gel and vacuum distilled in a 100-theoretical-plate column. Properties: b.p. 80.8° (32 mm); n_D^{20} 1.4910; d_4^{20} 0.8570. Literature data [8]: b.p. 177.10° (760 mm); n_D^{20} 1.4909; d_4^{20} 0.8573.

$\Delta \nu$ (cm^{-1}): 223 (25, sh); 258 (3); 274 (2); 302 (22, sh); 334 (2); 354 (5); 386 (14); 443 (37); 464 (4); 506 (3, sh); 542 (6); 563 (2); 609 (2); 644 (74); 666 (2); 688 (5, sh); 721 (13); 777 (5); 803 (150); 818 (86); 834 (5); 858 (3); 870 (2); 891 (23); 918 (3); 928 (3); 956 (17); 974 (3); 999 (7); 1019 (4); 1036 (3); 1058 (44); 1083 (4, sh. f); 1104 (29); 1142 (12); 1186 (45); 1208 (145); 1243 (3); 1279 (11); 1304 (26); 1343 (5, sh); 1379 (41); 1402 (5); 1410 (7, sh); 1441 (23); 1463 (35); 1532 (4, f); 1577 (11); 1612 (100); 1629 (27); 1664 (3, sh); 2867 (140); 2905 (70); 2924 (150); 2934 (100); 2965 (190); 3012 (70); 3030 (80, r); 3056 (100); 3152 (10); 3184 (10).

1,4-Diethylbenzene. Obtained from a technical mixture of diethylbenzenes, simultaneously with the 1,3-isomer (see below). From the higher-boiling fractions collected after removal of the 1,3-isomer on a 100-theoretical-plate column, an attempt was made to isolate the 1,4-diethylbenzene by means of chromatographing twice on large quantities of silica gel; however, as is evident from the spectra cited, this method was not successful in obtaining the compound in a sufficiently pure form (it contains ~7% of the 1,3-isomer). Therefore, the present spectrum is given as preliminary. Properties: b.p. 90.5° (37 mm); n_D^{20} 1.4949; d_4^{20} 0.8620. Literature data [8]: b.p. 183.752° (760 mm); n_D^{20} 1.49483; d_4^{20} 0.86196.

$\Delta \nu$ (cm^{-1}): 182 (30, sh); 196 (30, sh); 217 (10, sh); 258 (5); 301 (3); 326 (4); 363 (5); 381 (12, sh); 456 (8); 512 (5); 622 (2); 643 (62); 672 (4); 716 (7); 772 (5); 799 (140); 817 (43); 839 (10); 899 (2); 964 (31); 1001 (23); 1035 (4); 1063 (60); 1182 (72); 1199 (92); 1257 (7, sh); 1325 (23); 1375 (6); 1401 (2); 1447 (45); 1522 (4); 1576 (6, sh); 1613 (88); 2728 (20); 2858 (90); 2875 (100); 2900 (120); 2914 (130); 2934 (220); 2968 (140); 3012 (50); 3030 (50); 3053 (100).

1-Methyl-4^2-metho-4-butylbenzene. Obtained from p-xylene, purified by low-temperature crystallization (degree of purity 99.8%), and converted by chlorination to α-chloro-p-xylene. The latter, by a Grignard reaction with methyl ethyl ketone, was converted to 1-methyl-4^2-hydroxy-4^2-metho-4-butylbenzene, which then was dehydrated under the action of boric acid and hydrogenated in a with platinized carbon activated by chloroplatinic acid [13]. The 1-methyl-4^2-metho-4-butylbenzene obtained by this method was purified by vacuum distillation in a 100-theoretical-plate column. Properties: b.p. 92.5° (12.5 mm); n_D^{20} 1.4899; d_4^{20} 0.8582. This hydrocarbon has not been reported in the literature.

$\Delta \nu$ (cm^{-1}): 200 (5, sh); 257 (3, sh); 291 (8); 324 (40, sh); 365 (5); 384 (3); 437 (2); 456 (3); 492 (7, sh); 620 (3); 644 (58, r); 666 (4); 703 (15); 737 (3); 751 (5); 768 (24); 795 (12); 811 (17); 840 (64, sh); 913 (15); 940 (5); 979 (5); 1012 (7); 1032 (10); 1119 (15); 1151 (10); 1183 (33); 1202 (145); 1258 (8); 1281 (12); 1320 (14); 1348 (19); 1378 (37); 1415 (10, sh); 1445 (44, sh); 1462 (31); 1529 (6); 1589 (10, sh); 1616 (110); 2854 (140); 2872 (180, sh); 2911 60, f); 2920 (200); 2934 (50, f); 2963 (110); 3011 (80); 3028 (90); 3053 (120).

1,4-di-tert-Butylbenzene. Obtained by alkylation of benzene with isobutyl alcohol in the presence of concentrated sulfuric acid.

TABLE 1. Characteristic Lines in Spectra of Certain Benzenes with One Side Chain

Compound	Line, cm^{-1}						
	620	1000	1030	1155	1180	1200	1600
n-Butylbenzene [4]	624 (47)	1003 (265)	1033 (73)	1157 (29)	1181 (23)	1203 (66)	1606 (80)
sec-Butylbenzene [4]	623 (37), r	1002 (230)	1031 (77), r	1157 (25), r	1182 (22), r	1207 (54), r	1606 (70)
Isobutylbenzene	622 (44)	1004 (280)	1031 (78)	1157 (26)	1179 (21)	1206 (64)	1606 (64)
ter-Butylbenzene	622 (42)	1003 (300)	1033 (125)	1158 (22)	1192 (54)	1205 (54)	1604 (70)
2-Methyl-3-phenylpropene-1	621 (52), r	1004 (360), r	1031 (84), r	1155 (25)	1176 (41)	1194 (45); 1207 (26)	1603 (62, sh)
2-Methyl-1-phenylpropene-1	619 (54), r	1001 (600), r; 996 (170)	1030 (90), r	1155 (58), r	1182 (125)	1223 (380), r	1598 (960, sh)
Cyclohexylbenzene	622 (60)	1002 (170)	1030 (76)	1155 (22)	1180 (33)	1200 (62)	1602 (82)

TABLE 2. Characteristic Lines in Spectra of Certain 1,4-Dialkylbenzenes

Compound	Line, cm^{-1}			
	645	760—830	1200	1600
p-Xylene [2]	645 (75)	829 (270)	1205 (230)	1618 (120)
1-Methyl-4-ethylbenzene [2]	645 (75)	826 (190)	1202 (150)	1617 (110)
1-Methyl-4-isopropylbenzene	644 (74)	803 (150)	1208 (145)	1612 (100)
1, 4-Diethylbenzene	643 (62)	799 (140)	1199 (92)	1613 (88)
1, 4-Diisopropylbenzene [4]	642 (48)	780 (210)	1213 (72)	1616 (125)
1-Methyl-4^2-metho-4-butyl-benzene	644 (58,r)	Weak lines	1202 (145)	1616 (110)
1, 4-di-tert-Butylbenzene	645 (36)	743 (260)	1296 (60)	1614 (70)

Recrystallized several times from alcohol until the compound was obtained with f.p. 77.5°, unchanged on further recrystallization. Literature data [14]: f.p. 77.7°.

$\Delta \nu$ (cm^{-1}): 165 (100); 242 (58); 354 (8, sh); 371 (2); 389 (1); 458 (2, sh. f); 477 (6, sh); 518 (25); 592 (2); 617 (3); 645 (36); 710 (5); 743 (260, r); 795 (2); 817 (2); 850 (14); 923 (45); 932 (44); 1023 (4, sh); 1063 (3); 1097 (150); 1134 (2); 1162 (3); 1206 (60); 1271 (19); 1293 (3); 1320 (5); 1448 (33); 1468 (38); 1614 (70); 2712 (30); 2865 (90); 2907 (170); 2932 (120); 2956 (150, f); 2967 (250); 3015 (10); 3046 (30); 3068 (70).

1,3-Diethylbenzene. Isolated from a technical mixture of diethylbenzenes. Mixture was freed of unsaturated by bromination with Kaufman bromine solution [9] at room temperature. Then the vacuum-distilled preparation was chromatographed on silica gel and vacuum distilled in a 100-theoretical-plate column. Thereby the lower-boiling 1,3-diethylbenzene was separated from the higher-boiling 1,2- and 1,4-isomers. Properties: b.p. 87.5° (35 mm); n_D^{20} 1.4956; d_4^{20} 0.8640. Literature data [8]: b.p. 181.102° (760 mm); n_D^{20} 1.49552; d_4^{20} 0.86394.

$\Delta \nu$ (cm^{-1}): 146 (70, sh); 163 (80, sh); 198 (20, sh); 251 (3, sh); 265 (3, sh); 307 (4, sh); 325 (3, sh); 451 (8, sh); 479 (3); 500 (10, sh); 513 (20, sh); 552 (6); 586 (8); 620 (8, sh); 640 (3); 679 (3); 699 (10); 715 (110); 736 (3); 799 (10, sh); 839 (2); 866 (5); 914 (4); 964 (28); 985 (10, f); 1002 (310); 1020 (6); 1040 (12); 1064 (43); 1103 (14); 1146 (3, sh); 1171 (22); 1237 (43); 1267 (3); 1298 (4); 1327 (31); 1374 (10); 1442 (48); 1455 (42); 1589 (40); 1610 (66); 2854 (130); 2875 (170, f); 2896 (150, f); 2907 (170); 2936 (260); 2968 (210); 3003 (80); 3040 (90, sh); 3059 (150).

DISCUSSION OF THE EXPERIMENTAL RESULTS

Benzenes with one side chain. In the spectra of all compounds of the indicated type which were investigated, there are the characteristic lines which were noted previously [1], ~620, 1000, 1030, 1155, 1180, 1200, 1585 and 1605 cm^{-1}, the intensities of which vary, as a rule, within narrow limits (Table 1). It is curious that the line ~1000 cm^{-1}, which is always single for mono-substituted benzenes with aliphatic and alicyclic substituents, was found in the cyclohexylbenzene spectrum to be split into two, 996 and 1002 cm^{-1}, equal in intensity. In the spectrum of the cyclohexylbenzene there are also lines characteristic for monoalkylcyclohexanes in the regions 440, 840, and 1265 cm^{-1}. The other characteristic line of the cyclohexane ring ~1155 cm^{-1} does not stand out with sufficient clarity, owing to the proximity of one of the characteristic lines of monoalkylbenzenes. If the spectra of ethyl-, n-propyl-, n-butyl-, and isobutylbenzenes, on the one hand, are compared with those of isopropyl-, sec-butyl-, and cyclohexylbenzene, on the other hand, then it can be noted that for the first group there is a line ~490 cm^{-1} which is absent or very weak for the second group; at the same time, a line ~460 cm^{-1} is observed in the spectra of the second group which is not observed in the first group. Presumably this peculiarity may be connected with the presence of the general structural elements ⬡—CH$_2$— for the molecules of the first series and ⬡—CH⟨ for the molecules of the second series. At first it seemed that among the compounds of the first series there is an exception, n-hexylbenzene, since for this compound the 490 cm^{-1} line is not listed in a well-known atlas of Raman spectra [5]. However, in the work of Goubeau [15], such a line is indicated. This line, as a matter of fact, is also evident in the photograph of the n-hexylbenzene spectrum inserted in the atlas cited. Hence, n-hexylbenzene also is not an exception in the series of benzenes with one primary side chain. Thus, it appears possible to distinguish monoalkylbenzenes with primary and secondary groupings on the basis of general spectral criteria.
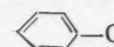
One should dwell in particular on the spectra of the isobutenylbenzenes, which are of not only practical, but also of theoretical interest. In the spectrum of the isomer in which the double bond is not conjugated with the ring (2-methyl-3-phenylpropene-1) all of the above-enumerated lines, which are characteristic for monosubstituted benzene homologs, are observed, and their intensities are close to normal. The frequency and intensity of the double-bond line also have normal values. In the spectrum of the other isomer (2-methyl-1-phenylpropene-1), where the double bond is conjugated with the benzene ring, certain characteristic lines of the monosubstituted benzenes and the line of the double bond are sharply intensified. It is interesting that there is also an intensification of the lines in the region ~ 1450 cm^{-1}, which usually are interpreted as deformation vibrations of CH_2- and CH_3- groups. In the spectra of conjugated dienes these lines are not intensified. We note that in the spectrum of this isomer relatively intense lines appear at 837 and 1493 cm^{-1}, which are absent for monoalkylbenzenes. It appears probable that the 1493 cm^{-1} line is caused by the vibration which is responsible for the appearance of an intense band ~ 1500 cm^{-1} in the infrared spectra of benzene and alkylbenzenes. Although this vibration is also allowable in the Raman spectra of alkylbenzenes (in the case of benzene itself it is prohibited by the rule of selectivity), but the corresponding line for the alkylbenzenes either is very weak or is completely absent. The intensification of this line in the spectrum of the isomer under consideration apparently is caused by the conjugation. At the same time, it must be noted that the conjugation does not lead to a sharp intensification of all of the characteristic lines of the monoalkylbenzenes; such lines as 623, 1000, 1030, and 1575 cm^{-1} either show practically no intensification or comparatively little (the greatest increase in intensity, approximately twofold, is observed for the 1001 cm^{-1} line).

The intensity of the lines of the valence vibrations of the $C-H$ bonds for the conjugated isomer are unchanged, which is in accord with the literature data [16].

p-Dialkylbenzenes. In the spectra of the p-dialkylbenzenes almost all of the lines are present that were noted previously [1] as characteristic for this type of alkyl substitution of the benzene ring. The exception is 1-methyl-4^2-metho-4-butylbenzene, in whose spectrum the intense line in the 700-830 cm^{-1} region is absent (Table 2). The data obtained here confirm the gradual decrease in frequency noted in previous work for the intense line of p-xylene at 829 cm^{-1}, the decrease being in proportion to the size of the substituents: in the spectrum of 1,4-di-tert-butyl-benzene it reaches a value of 743 cm^{-1}. Thus, taking into account the data of the present work, the most characteristic group criteria of the 1,4-dialkylbenzenes should be considered as the line ~ 645 cm^{-1}, the average intensity of which for $C_{10}H_{14}-C_{12}H_{18}$ aromatics constitutes ~ 60 units. An additional criterion for this series is also the somewhat increased value of frequency of the line in the region ~ 1600 cm^{-1}, from the normal value ~ 1605 up to 1612-1616 cm^{-1}.

1,3-Diethylbenzene. The spectrum of this hydrocarbon once again shows that the line ~ 525 cm^{-1}, contrary to our previous opinion, is not sufficiently characteristic for the series of 1,3-dialkylbenzenes. We had already drawn such a conclusion previously [4] in the example of 1,3-diisopropylbenzene. Further, the line in the 1250 cm^{-1} region which is present in the spectra of the previously studied 1,3-dialkylbenzenes [1] is shifted for 1,3-diethyl-benzene in the direction of lower frequencies, and therefore it likewise cannot be considered as sufficiently reliable for identification of the series under consideration. Apparently the most characteristic group criterion of the series of 1,3-dialkylbenzenes is the line ~ 1000 cm^{-1}, even though it is also observed in the spectra of monoalkyl- and 1,3,5-trialkylbenzenes.

The authors take the opportunity to express their gratitude to E. M. Terent'eva for the obligingly furnished preparation of cyclohexylbenzene.

SUMMARY

1. The characteristic group spectral criteria established previously for benzenes with one side chain have been confirmed, and the possibility of distinguishing primary and secondary radicals has been demonstrated.

2. The line ~ 645 cm^{-1} is the most characteristic group criterion for 1,4-dialkylbenzenes.

3. The existing group criteria for 1,3-dialkylbenzenes were found to be insufficiently characterisitic.

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COMBINATION DISPERSION [RAMAN] SPECTRA OF CERTAIN TRI- AND TETRAALKYLBENZENES AND CONDENSED AROMATIC HYDROCARBONS

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In our preceding communication [1] spectra were listed for ten benzene-series hydrocarbons with one or two side chains, boiling above 150°. The investigation was conducted for defining more precisely a method proposed earlier [2] for determining the narrow-group composition of ligroin fractions. This determination is carried out on the basis of characteristic lines established for various types of substitution of the benzene ring. Unfortunately, in a number of cases the frequencies and intensities of the characteristic lines were derived in the cited work from a small number of spectra. For example, the criteria for 1,3,5-trialkylbenzenes were established from an examination of the only two spectra known at that time for hydrocarbons of this type, mesitylene and 1,3-dimethyl-5-ethyl-benzenes; moreover, the spectrum of the latter compound was obtained by a method of photoelectric recording with a wide aperture [3], i.e., by a method having definite shortcomings [4, 5]. For this it appeared necessary to define more precisely the narrow-group criteria on 1,3-dimethyl-5-ethylbenzene and other objects of study. The spectral analysis of ligroins is also hindered by the absence of reliable data on the spectra of even the simplest condensed-ring aromatic hydrocarbons and their immediate homologs. It is sufficient, for example, to point out that a different times six spectra have been published for tetralin differing from each other considerably [6]. For homologs of indan, there is known only the spectrum of α-methylindan, where the intensity of the lines was estimated visually on a ten-point scale. The frequencies of the lines in the spectra of naphthalene and the methylnaphthalenes are well known; however, their intensities have been measured only by the photoelectric method with a wide aperture [3].

The present communication is aimed at filling in these gaps to some degree. Here spectra are listed for three 1,3,5-trialkylbenzenes, two compounds representing other types of benzene substitution (1,2,4 and 1,2,3,5), and five aromatic hydrocarbons with condensed rings. These hydrocarbons were purified very carefully, as indicated below. The method of obtaining the spectra and their measurements were described previously [7]. All of the spectra were obtained for the liquid state of the substance; the majority were obtained at room temperature, but the spectrum of the naphthalene was obtained on the melt at ~90°.

EXPERIMENTAL

1,3-Dimethyl-5-ethylbenzene. Obtained from m-xylene by alkylation with ethyl bromide in the presence of aluminum chloride. The 1,3-dimethyl-5-ethylbenzene was purified by chromatography on large quantities of silica gel, and then vacuum distilled in a 100-theoretical-plate column. Properties: b.p. 87.6° (32 mm); n_D^{20} 1.4981; d_4^{20} 0.8642. Literature data [8]: b.p. 183.75° (760 mm); n_D^{20} 1.4981; d_4^{20} 0.8648.

$\Delta \nu$ (cm^{-1}): 146 (60, f); 172 (10, sh); 208 (70, f); 231 (90); 272 (31); 325 (5, f); 353 (4, f); 386 (2, f); 426 (3); 505 (25); 516 (72); 556 (115); 584 (3); 604 (46); 703 (2); 851 (1, sh); 887 (7); 970 (5, sh); 1000 (270); 1022 (3, f); 1035 (25); 1065 (12); 1165 (12); 1203 (1); 1244 (1); 1291 (49); 1331 (38); 1379 (72); 1444 (20, sh); 1460 (15, sh); 1494 (3); 1530 (3); 1581 (2); 1606 (64); 2729 (20); 2860 (120); 2873 (11); 2919 (320); 2932 (240); 2967 (150); 3005 (110); 3016 (110); 3069 (15); 3163 (5).

1,3,5-Triethylbenzene. Synthesized by alkylation of benzene with ethyl bromide in the presence of aluminum chloride; purified by chromatography on a large quantity of silica gel, and then by vacuum distillation in a 100-theoretical-plate column. Properties: b.p. 98.6° (16.5 mm); n_D^{20} 1.4958; d_4^{20} 0.8631. Literature data [9]: b.p. 217.5° (760 mm); m.p. −67.1°; n_D^{20} 1.4958; d_4^{20} 0.8633; degree of purity 99.0-99.5%.

$\Delta\nu$ (cm^{-1}): 162 (110, sh. f); 190 (10, sh. f); 301 (6, sh. f); 325 (6, sh. f); 468 (3); 483 (1); 518 (21); 541 (16); 582 (7); 620 (3); 642 (5); 675 (1); 705 (1); 781 (8); 883 (12); 962 (26); 1000 (260); 1064 (50); 1103 (3); 1165 (5); 1188 (2); 1250 (7); 1271 (25); 1318 (10, sh); 1342 (48); 1374 (14); 1442 (52); 1456 (47); 1493 (1); 1602 (58); 2856 (100, f); 2877 (150, f); 2896 (170, f); 2907 (170, f); 2936 (280); 2967 (200); 3006 (90); 3015 (70); 3067 (30, sh).

1,3-Dimethyl-5-tert-butylbenzene. Obtained by interaction of m-xylene with trimethyl carbinol [tert-butyl alcohol] in the presence of aluminum chloride, and purified by chromatography on large quantities of silica gel and by vacuum distillation in a 100-theoretical-plate column. Properties: b.p. 108.3° (33 mm); f.p. −17.4°; n_D^{20} 1.4962; d_4^{20} 0.8654. Literature data [9]: b.p. 209° (760 mm); m.p. −18.3°; n_D^{20} 1.4965; d_4^{20} 0.8652. It may be considered that the constants which we have cited are the more reliable.

$\Delta\nu$ (cm^{-1}): 169 (7); 183 (10); 204 (62); 228 (52); 258 (33); 280 (3); 307 (26); 325 (5, sh. f); 349 (13); 402 (8, sh); 489 (18); 513 (28); 527 (42, dv); 567 (165, r); 598 (15); 708 (4); 790 (39); 875 (5, sh); 889 (7); 902 (31); 927 (31); 933 (20, f); 998 (170); 1030 (29); 1140 (11); 1152 (5, f); 1166 (7); 1202 (30, sh); 1227 (14); 1259 (3, f); 1273 (4, f); 1302 (54); 1346 (3, f); 1362 (2, f); 1378 (50); 1410 (5, sh. f); 1428 (10, sh. f); 1444 (32); 1464 (28); 1475 (8, f); 1523 (2, sh); 1572 (2, sh); 1604 (62); 2861 (110); 2899 (260); 2916 (290); 2929 (310); 2952 (210); 2970 (220); 3007 (90); 3044 (60).

1,4-Dimethyl-2-ethylbenzene. p-Xylene, purified by multiple recrystallizations from ether at low temperature, was brominated to 2-bromo-p-xylene. By the action of diethyl sulfate on the organomagnesium derivative of this bromide, 1,4-dimethyl-2-ethylbenzene was obtained; this was purified by chromatography on silica gel, vacuum distillation, and additional chromatography. Properties: b.p. 104.5° (57 mm); n_D^{20} 1.5043; d_4^{20} 0.87772. Literature data [8]: b.p. 186.91° (760 mm); n_D^{20} 1.5043; d_4^{20} 0.8772.

1,2,3,5-Tetramethylbenzene (Isodurene). Mesitylene, freed from unsaturates by bromination with Kaufman bromine solution [10] and then purified by chromatogrp

$\Delta\nu$ (cm^{-1}): 148 (40, sh); 169 (10, sh); 281 (15); 296 (15); 324 (10, sh); 346 (20, sh); 437 (10); 461 (33); 471 (56); 540 (76); 562 (2); 599 (15); 712 (82, r); 737 (80); 755 (23); 798 (15); 810 (8); 883 (0); 902 (50, sh); 947 (2); 967 (15); 1002 (18, sh); 1033 (4, dv); 1052 (1); 1066 (22); 1104 (2); 1131 (12); 1159 (10); 1211 (11); 1240 (115); 1285 (4); 1298 (3); 1324 (23); 1380 (76); 1452 (47, sh. dv); 1500 (3); 1580 (28, sh); 1619 (90); 2863 (90); 2873 (90); 2895 (60, f); 2918 (170, sh. f); 2936 (140, sh. f) 2969 (90, f); 2993 (50, f); 3047 (70, sh); 3081 (10).

1,2,3,5-Tetramethylbenzene (Isodurene). Mesitylene, freed from unsaturates by bromination with Kaufman bromine solution [10] and then purified by chromatography, was brominated to 2-bromomesitylene. By the action of dimethyl sulfate on the organomagnesium derivative of this bromide, isodurene was obtained; this was purified by chromatography on large quantities of silica gel and by vacuum distillation in a 100-theoretical-plate column. Properties: b.p. 88.8° (20 mm); f. p. −23.7°; n_D^{20} 1.5131; d_4^{20} 0.8903. Literature data [8]: b.p. 198.00° (760 mm); f.p. −23.685°; n_D^{20} 1.5130; d_4^{20} 0.8903.

$\Delta\nu$ (cm^{-1}): 197 (3); 232 (80); 276 (25); 328 (62); 453 (66); 494 (8); 514 (29); 546 (54); 573 (250); 616 (2); 703 (4); 734 (78); 880 (5); 928 (3); 958 (66); 1033 (4, sh); 1110 (3, sh. f); 1143 (52); 1170 (6, f); 1211 (18); 1255 (4); 1294 (110); 1380 (92); 1409 (8, sh); 1442 (22); 1483 (12); 1523 (3); 1579 (15); 1613 (70); 2859 (150); 2910 (300, sh); 2943 (140, f); 2970 (90, f); 3009 (100); 3044 (20).

1-Methylindan. By the action of aluminum chloride on hexahydrocinnamyl chloride [11], indanone-1 was obtained; this with methylmagnesium iodide gave 1-methylindanol-1. The latter, after dehydration to 1-methyl-indene and hydrogenation over palladinized carbon activated with palladium chloride [12], gave 1-methylindan, which was then purified by vacuum distillation in a 100-theoretical-plate column. Properties: b.p. 120.3° (100 mm); n_D^{20} 1.5262; d_4^{20} 0.9406. Literature data [13]: b.p. 189.5° (739.2 mm); n_D^{25} 1.5241; d_4^{25} 0.9384.

$\Delta\nu$ (cm^{-1}): 146 (60, sh); 164 (60, sh); 215 (30, sh); 264 (15, sh); 290 (6); 332 (3); 364 (3); 391 (7); 413 (8); 449 (17); 509 (64, r); 527 (52); 583 (17); 606 (11); 635 (3); 654 (5); 716 (20); 735 (100, r); 753 (44); 767 (15); 801 (12); 842 (35); 864 (8); 1013 (120); 1025 (100, r); 1066 (3, sh); 1080 (5, sh); 1105 (5, sh); 1154 (40); 1163 (15); 1190 (29); 1211 (54, sh); 1257 (5, f); 1269 (20); 1300 (6); 1328 (30, sh); 1436 (43, r); 1456 (52); 1584 (38, r); 1606 (43); 2845 (170); 2867 (130); 2886 (90); 2902 (110); 2925 (130); 2955 (160, sh. dv); 3011 (20); 3033 (150); 3046 (190); 3071 (80).

TABLE 1. Characteristic Lines of 1,3,5-Trialkylbenzenes

Compound	Parameters of characteristic lines							
	cm^{-1}	I_0	cm^{-1}	I_0	cm^{-1}	I	w	I
Mesitylene [5]	517	170	578	310	999	250	1301	100
1,3-Dimethyl-5-ethylbenzene	516	72	556	115	1000	270	1291	49
1,3-Dimethyl-5-tert-butyl-	513	28	567	165	998	170	1302	54
benzene	527	42						
1,3,5-Triethylbenzene	518	21	541	16	1000	260	1271	25
Previously published averaged data	513	120*	574	120*	999	350*	1297	100*

* The average values of intensities presented here from the previously cited work [2] were obtained as a result of utilizing insufficiently accurate literature data and were found to be approximately 40% high.

2-Methylindan. Obtained by C_5-dehydrocyclization of isobutylbenzene at 310° on platinized carbon [12], separated from the catalyzate by vacuum distillation in a 30-theoretical-plate column, and then twice chromatographed on silica gel. In view of the small quantities of material subjected to purification, it was hardly expected that it would serve the purpose adequately. Indeed, an examination of the spectrum shows that the preparation contains 6-7% of monoalkyl- and alkenylbenzenes, including 3-4% of 2-methyl-1-phenylpropene-1. Therefore, the spectroscopic data shown here should be regarded as preliminary. Properties: b.p. 118.7-119.2° (100 mm); n_D^{20} 1.5225; d_4^{20} 0.9300. The literature data on the constants of 2-methylindan are very contradictory [13, 14].

$\Delta \nu$ (cm^{-1}): 167 (60, sh); 189 (30, sh); 209 (3, f); 248 (40, sh); 281 (3); 304 (3); 333 (2); 365 (8); 381 (4); 406 (15); 415 (10); 450 (2); 509 (3); 530 (30); 584 (34); 620 (10); 653 (2); 689 (7, sh); 740 (20, sh); 775 (70); 793 (50); 808 (10, f); 836 (48, sh); 859 (7); 896 (8); 909 (8); 937 (10, sh); 1000 (30, r); 1024 (190); 1040 (5, f); 1066 (3); 1088 (18); 1151 (31); 1181 (2); 1203 (75); 1222 (40); 1250 (12, sh); 1265 (12, sh); 1316 (27); 1344 (5); 1378 (12); 1437 (78, dv); 1456 (52); 1490 (3); 1584 (42, r); 1600 (60, r); 1607 (60, r); 1657 (36); 2838 (150, sh); 2869 (140); 2898 (180, sh. f); 2928 (290, sh); 2956 (170, sh); 3004 (40); 3042 (400, sh); 3073 (140); 3157 (30).

Tetralin. Naphthalene, previously purified by boiling in the melt with metallic sodium until a negative sulfur reaction was obtained, was hydrogenated in an autoclave with Raney nickel at 190-200° and hydrogen pressure 10-15 atm. The tetralin which was obtained was vacuum distilled in a 30-theoretical-plate column. Properties: b.p. 92.7-92.8° (20 mm); n_D^{20} 1.5414; d_4^{20} 0.9702. Literature data [8]: b.p. 207.57° (760 mm); n_D^{20} 1.54135; d_4^{20} 0.9702.

$\Delta \nu$ (cm^{-1}): 158 (100); 166 (70); 262 (50); 308 (4, sh); 397 (3); 431 (74); 453 (25); 502 (28); 580 (73); 603 (4); 643 (2); 700 (26); 724 (240); 742 (10, f); 785 (3); 805 (29); 817 (38); 865 (15); 895 (3); 901 (4); 982 (18, sh. dv); 1006 (5); 1037 (270); 1067 (27); 1078 (17); 1112 (12); 1158 (30); 1178 (2); 1201 (125); 1235 (12); 1249 (2); 1285 (31); 1295 (35); 1341 (34); 1355 (23,r); 1431 (80); 1448 (47); 1458 (25); 1580 (39); 1602 (80); 2838 (110); 2861 (130); 2883 (120); 2914 (140, sh); 2940 (200, sh); 2981 (15); 3025 (70); 3043 (130); 3060 (60); 3076 (40).

Naphthalene. Commerical material was recrystallized from alcohol and twice sublimed, which was sufficient to give no further change in melting point (80.1°). Literature data [8]: f.p. 80.290°.

$\Delta \nu$ (cm^{-1}): 371 (15); 387 (50); 433 (10); 477 (10); 511 (540); 617 (10); 719 (30); 739 (10); 761 (530); 774 (115); 879 (15); 942 (40, sh); 970 (38); 1026 (280); 1126 (10); 1145 (58); 1162 (15); 1207 (15); 1239 (56); 1340 (25); 1377 (2050); 1435 (60, sh. dv); 1459 (300, r); 1576 (270); 1628 (20); 1669 (5, sh); 2716 (15); 2862 (10); 2916 (10); 2948 (20); 2973 (40); 3004 (90); 3027 (110); 3047 (270); 2059 (570); 3090 (40); 3150 (20); 3190 (30); 3251 (70).

1-Methylnaphthalene. Commerical 1-bromonaphthalene was converted by a Grignard reaction with dimethyl sulfate to 1-methylnaphthalene, which was purified by chromatography on large quantities of silica gel and vacuum distilled in a 100-theoretical-plate column. Properties: b.p. 121.8° (18.5 mm); f.p. −30.4°; n_D^{20} 1.6175; d_4^{20} 1.0200. Literature data [8]: b.p. 244.642° (760 mm); f.p. −30.57°; n_D^{20} 1.6174; d_4^{20} 1.02015.

$\Delta \nu$ (cm^{-1}): 148 (100, sh. f). 253 (70, sh); 283 (30, sh); 309 (20, sh); 376 (15); 410 (40); 437 (78); 477 (135); 510 (300); 567 (240); 589 (10); 623 (10); 676 (10); 701 (640); 731 (25); 760 (10); 791 (15); 833 (10); 860 (100); 897 (20); 949 (15); 977 (72); 1019 (200); 1038 (25, f); 1061 (30); 1077 (155); 1101 (10); 1116 (15); 1140 (56); 1163 (52); 1185 (5); 1200 (10); 1213 (10); 1239 (40); 1264 (15); 1340 (20); 1358 (20, f); 1368 (700); 1377 (1200); 1400 (68); 1428 (115); 1440 (30, f); 1463 (145); 1507 (20); 1559 (20); 1580 (360); 1589 (270); 2857 (140); 2908 (130); 2931 (70); 2948 (50); 2980 (70); 3011 (130); 3039 (150); 3058 (660).

TABLE 2. "Characteristicness" [Specificity] of Criteria of Quaternary Carbon Atom in Spectra of Alkylbenzenes

Hydrocarbon	Presence of intense lines in region	
	900—950 cm^{-1}	680—750 cm^{-1}
tert-Butylbenzene [1]	931(35)	707(155)
Monoalkylbenzenes [2]	—	730—750 (50)*
1-Methyl-2-tert-butyl-benzene [17]	925 (60); 947 (20)	680 (200)**
1,2-Dialkylbenzenes [2]	—	714±3 (130)
1-Methyl-3-tert-butyl-benzene [17]	925 (24)	691 (180)
1,3-Dialkylbenzenes [2]	—	716±8 (140)
1-Methyl-4-tert-butyl-benzene [17]	922 (42); 932 (16); 943 (26)	—***
1,4-di-tert-Butylbenzene[1]	923 (45); 932 (44)	743 (260)****
1,4-Dialkylbenzenes [2]	—	780—810 (250)*****
1,3-Dimethyl-5-tert-Butyl-benzene	927 (31); 933 (20)	—
1,3,5-Trialkylbenzenes [2]	—	—

* This line was not included previously in the list of characteristic criteria of monoalkylbenzenes [2], owing to the inconstancy of frequency and, together with this, the relatively low intensity, even though it is present in all spectra known to us for hydrocarbons of this class.

** We have recalculated to the cyclohexane scale the intensities of the lines of hydrocarbons taken from the literature [17].

*** In the spectrum there is a line 796 (250) which is characteristic for 1,4-dialkylbenzenes.

**** This line is not constant in frequency, and is shifted in the direction of lower frequencies in proportion to the size of the substituents [4].

***** This line should undoubtedly be considered as a shifted characteristic line of 1,4-dialkylbenzenes.

DISCUSSION OF THE EXPERIMENTAL RESULTS

1,3,5,-Trialskylbenzenes. A comparison of the data obtained here with the spectrum of mesitylene [5] shows that the line ~1000 cm^{-1} is essentially the sole line whose frequency and intensity are sufficiently constant from the point of view of utilization in the method of narrow-group analysis. The parameters of the other lines of the 1,3,5-trialkylbenzenes [2], for example, in the 500-600 cm^{-1} and 1250-1300 cm^{-1} regions, vary over a considerable range (Table 1), which makes them practically inapplicable for narrow-group analysis. However, the line ~1000 cm^{-1}, as is well known, is also present in the spectra of mono- and 1,3-dialkylbenzenes, and therefore it cannot always be utilized for analysis. Thus, in the spectra of the 1,3,5-trialkylbenzenes there are apparently no lines which are characteristic solely for this type of benzene-ring substitution and suitable for performing narrow-group analysis. On the other hand, the spectra of the 1,3-dimethyl-5-dialkylbenzenes are considerably more similar to each other and differ markedly from the 1,3,5-triethylbenzene (Table 1). Evidently the similarity is caused by the presence of the methyl substituents in positions 1 and 3, which is general for these compounds. The replacement of the two methyl groups by ethyl leads to a substantial change of the spectrum (compare spectra of 1,3-dimethyl-5-ethylbenzene and 1,3,5-triethylbenzene). Thus, we encounter the fact that the influence of the nature of the alkyl substituents on the vibrational spectrum of the ring is more significant than had been assumed previously, in particular for types more complex than the dialkylbenzenes. Furthermore, even in the case of the dialkylbenzenes the role of the nature of the radicals is already noticeable. However, for the monoalkylbenzenes the structure of the side chain has practically no influence on the position and intensity of their principal characteristic lines, and affects only the finer details. The picture is apparently analogous for other series of hydrocarbons containing one ring or

another as the common structural element, for example, for homologs of cyclopentane and cyclohexane. At the same time, such features of the spectra may be basic for a finer classification of spectral criteria; they make it possible to establish not only the type of benzene ring substituion, but also the nature of the alkyl substituents. Of course, for this purpose measurements of spectra will be necessary for a wider range of model compounds.

1,4-Dimethyl-2-ethylbenzene. The spectrum of this hydrocarbon contains all of the lines noted previously as characteristic for 1,2,4-trialkylbenzenes [2], but the lines are somewhat shifted in the direction of lower frequencies and are less intense. Thus, the line in the 548 ± 6 cm^{-1} region, for which an average intensity of 120 units had been deduced previously [2], is notably weaker (76 units) in the spectrum of the 1,4-dimethyl-2-ethylbenzene. Hence, it follows that further refinement is necessary for the average values of the intensities of the characteristic lines chosen for benzene homologs of the type under consideration. This is dictated all the more by the fact that the spectral criteria were established previously on the example of only four of the simplest representatives of this series, namely, pseudocumene [5], 1,4-dimethyl-2-ethylbenzene [3], 1,3-dimethyl-4-ethylbenzene [3], and 1,2-dimethyl-4-ethyl-benzene [3],i.e., on compounds which always have two methyl groups as substituents, although at different positions.

Isodurene. Previously [4] spectra were given for three hydrocarbons of the 1,3,5-trimethyl-2-alkylbenzene series. The first member of this series, isodurene, has in its spectrum all of the characteristic lines of the 1,2,3,5-tetrasubstituted benzene [4]. However, it should be recalled that certain lines which were previously considered characteristic for 1,3,5-trialkylbenzenes proved to be, in reality, group criteria only for 1,3-dimethyl-5-alkyl-benzenes. The possibility of the occurrence of an analogous phenomenon for the 1,2,3,5-tetraalkylbenzenes is not excluded. All of the 1,2,3,5-tetrasubstituted derivatives investigated up to the present are essentially 1,3,5-tri-methyl-2-alkylbenzenes, and perhaps the established spectral criteria characterize in the first place just this nar-rower series of compounds. It is possible, certainly, that these lines are also characteristic for the more complex members of the 1,2,3,5-tetraalkylbenzene series, but such an assumption still requires additional confirmation.

Condensed-ring aromatic hydrocarbons. In the position of certain intense lines, the spectra of the two methyl-indans which were studied are similar to the spectrum of indan itself [3]. The following are thus common to the three spectra: 1025 cm^{-1} line (in the 1-methylindan spectrum there is still another intense line at 1012 cm^{-1}), the lines in the 500-600 and 1200-1300 cm^{-1} regions, and also several others. Along with this, the spectra of the 1- and 2-methylindans also have marked differences, although for the present it is impossible to decide whether they are characteristic for the 1- and 2-alkylindan series, owing to the absence of material. We note also a great resemblance of the spectra of tetralin and the dimethylindans and also that of indan itself to the spectra of 1,2-dialkylbenzenes: in both cases, intense lines are observed ~580, 1030, and 1200-1220 cm^{-1}. However, for tetraline* the frequency of the 1037 cm^{-1} line is markedly greater than for the indans (1024-1026 cm^{-1}) and closer to the frequency of the corresponding line of the 1,2-dialkylbenzenes. In contrast to the indan, the line in the 520-530 cm^{-1} region is absent for tetralin. Since this line as a rule is also absent from the spectra of 1,2-di-alkylbenzenes, it can be assumed that closing the side chains in the latter, forming a six-membered ring, introduces less change in the vibrational spectrum of the aromatic ring than occurs on the formation of a five-membered ring.

There are relatively few lines in the Raman spectra of naphthalene and 1-methylnaphthalene, but as a rule they are very intense. The data of our frequency measurements for naphthalene agree best of all with the results of an investigation published comparatively recently by Person and others [15].

Spectroscopic criteria of the quaternary carbon atom. In 1953 Sushchinskii [16] pointed out spectroscopic criteria which are characteristic for the quaternary carbon atom; he observed them in the instance of a large num-ber of paraffinic hydrocarbons, and also in certain cyclanes and open-chain olefins. He termed the intense lines in the 680-750 and 900-950 cm^{-1} regions as the most characteristic criteria. We now have available sufficient data to judge to what degree these conclusions can be carried over to aromatic hydrocarbons. Examining the spectra available to us for aromatic hydrocarbons with a quaternary carbon atom, we see that the intense line in the 680-750 cm^{-1} region appears only in those cases in which the given type of benzene-ring substitution is in general characterized by the presence of an intense line in this region, independent of whether or not a quaternary carbon atom is present in the side chains (Table 2). The role of such an atom consists only of the fact that the corre-sponding characteristic lines of a given type of substitution are shifted toward the region of lower frequencies and

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* We point out that our spectrum of tetralin is closest of all (with respect to position of the lines) to the data ob-tained by Saksena [6], although there are also certain deviations; moreover, we detected several new lines, in-cluding some rather intense ones (10-20 units).

are somewhat intensified. There is no intense line at all in this region of the spectrum of 1,3-dimethyl-5-tert-butylbenzene, just as there is none in the other known spectra of 1,3,5-trialkylbenzenes. Thus, the presence of a line in the 680-750 cm^{-1} region cannot be considered as a characteristic criterion of the quaternary carbon atom in all cases. At least, it is inapplicable to a quaternary carbon atom connected directly to a benzene ring.

The other criterion of the quaternary atom pointed out by Sushchinskii, the line in the 900-950 cm^{-1} region, is present in all of the spectra under consideration. In the absence of a quaternary carbon atom, there is no such line in the spectra.

SUMMARY

1. The "characteristicness" [specificity] of criteria of certain tri- and tetraalkylbenzenes has been examined and made more precise.

2. One of the previously proposed spectral criteria of the quaternary carbon atom, the intense line in the 680-750 cm^{-1} region, is not preserved in the spectra of aromatic hydrocarbons with such an atom. The other criterion, the line in the 900-950 cm^{-1} region, retains its "characteristicness" [specificity] in the benzene series.

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ORGANIC AND BIOLOGICAL CHEMISTRY

ADDITION OF BENZENETHIOL TO 2-CYANOVINYL KETONES

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The 2-cyanovinyl ketones that we prepared previously [1] are 3-acylacrylonitriles and have been studied very little, particularly in the case of the difficultly accessible 3-alkanoylacrylonitriles. An investigation of the properties of the 2-cyanovinyl ketones that have become available as a result of the synthesis developed by us on the basis of 2-chlorovinyl ketones is therefore of interest. We showed that 2-cyanovinyl ketones contain a double bond that is active toward nucleophilic reagents [2].

In the present work we investigated the conditions for the reaction of 2-cyanovinyl ketones with benzenethiol. It was found that alkyl 2-cyanovinyl ketones undergo addition with benzenethiol at the double bond on simple mixing of the reactants in ether solution, when reaction proceeds with evolution of heat. In the case of 2-cyanovinyl phenyl ketone the reaction with benzenethiol is slow, but is accelerated by traces of alkali:

$$RCOCH{=}CHCN + HSC_6H_5 \longrightarrow RCOCH_2CHCN \\ \qquad\qquad\qquad\qquad\qquad\qquad | \\ \qquad\qquad\qquad\qquad\qquad\qquad SC_6H_5$$
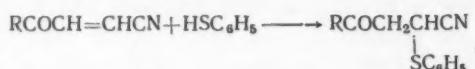
in which $R = CH_3$, $n\text{-}C_3H_7$, C_6H_5.

The yields of the 3-acyl-2-(phenylthio)propionitriles were almost quantitative. 3-Acyl-2-(phenylthio)propionitriles are almost colorless crystalline substances; their structure was confirmed by the hydrolysis of 3-benzoyl-2-(phenylthio)propionitrile into the corresponding acid.

However, we did not succeed in hydrolyzing this nitrile to the acid in one stage. Under the action of alkaline reagents the nitrile underwent some complex transformations which did not lead to the formation of the acid. When the nitrile was treated with concentrated sulfuric acid in the cold the hydrolysis went as far as the amide, though this was obtained in very low yield and in a highly contaminated state. The hydrolysis of the nitrile to the amide stage was effected with the best results by the use of 70% perchloric acid. The resulting amide was converted by very careful treatment with nitrous acid into the already described 3-benzoyl-2-(phenylthio)propionic acid [3].

$$C_6H_5COCH_2CHCN \xrightarrow{HClO_4} C_6H_5COCH_2CHCONH_2 \xrightarrow{HNO_2} C_6H_5COCH_2CHCOOH \\ \quad\quad\quad | \qquad\qquad\qquad\qquad\qquad | \qquad\qquad\qquad\qquad\qquad\qquad | \\ \quad\quad SC_6H_5 \qquad\qquad\qquad\qquad SC_6H_5 \qquad\qquad\qquad\qquad\qquad SC_6H_5$$
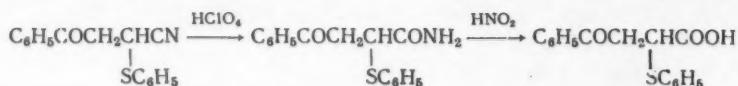
The presence of vibration frequencies at 1700 cm^{-1} in the infrared spectra of 3-benzoyl- and 3-acetyl-2-(phenylthio)propionitriles confirms the presence of the C = O group in these compounds. Hence, benzenethiol adds to 2-cyanovinyl ketones in a way analogous to that in which it adds to amines [2], so that the carbonyl group has the strongest orienting action.

In alcoholic solution 3-benzoyl-2-(phenylthio)propionitrile readily gives a double salt with silver nitrate (decomp. temp. 126-127°), which rapidly decomposes into the original substances when heated in an aqueous medium. 3-Acyl-2-(phenylthio)propionitriles may be oxidized with hydrogen peroxide to the corresponding sulfones in good yield:

$$RCOCH_2CH{-}CN \xrightarrow{H_2O_2} RCOCH_2{-}CH{-}CN \\ \qquad\quad | \qquad\qquad\qquad\qquad\qquad\qquad | \\ \qquad SC_6H_5 \qquad\qquad\qquad\qquad\qquad SO_2C_6H_5$$

$$\underset{\underset{O}{\|}\ \ \underset{X}{|}}{R C C H_2 C H C N}$$
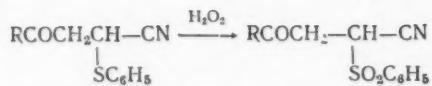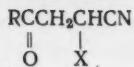
R	X	M.p. (°C)	Yield (%)	Analytical figures (%)							
				C		H		N		S	
				found	calc.	calc.	found	calc.	calc.	found	calc.
CH_3	C_6H_5S	34—34,5	90	64,20	64,36	5,38	5,40	6,79	6,82	15,62	15,62
n-C_3H_7	C_6H_5S	35,5—36	84	66,95	66,89	6,40	6,48	6,12	6,00	13,66	13,75
C_6H_5	C_6H_5S	62—63	85	71,86	71,88	4,90	4,90	5,40	5,24	11,96	11,99
CH_3	$C_6H_5SO_2$	116	65	55,50	55,68	4,50	4,67	5,82	5,90	13,41	13,51
n-C_3H_7	$C_6H_5SO_2$	64	70	58,83	58,84	5,74	5,69			12,14	12,09
C_6H_5	$C_6H_5SO_2$	151	80	64,07	64,13	4,32	4,38	4,72	4,68	10,67	10,71

These are more stable in recrystallization than the original sulfides. On treatment of 3-benzyl-2-(phenylsulfonyl)-propionitrile with alkali, benzenesulfinic acid is eliminated and 2-cyanovinyl phenyl ketone is recovered in 80% yield. The sulfinic acid was identified by its reaction with mercuric chloride [4].

$$\underset{\underset{SO_2C_6H_5}{|}}{C_6H_5COCH_2CH-CN} \xrightarrow{\text{NaOH}} C_6H_5COCH=CH-CN+HSO_2C_6H_5$$
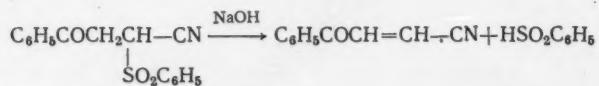
The elimination of the sulfinic acid proves conclusively that in the oxidation of 3-acyl-2-(phenylthio)propionitriles with hydrogen peroxide it is the sulfur atom that is oxidized.

EXPERIMENTAL

Addition of benzenethiol to 2-cyanovinyl ketones. Benzenethiol (0.02 mole) was added to an ether solution of 0.02 mole of the 2-cyanovinyl ketone. The mixture was left at room temperature for one day. Solvent was evaporated off, and the residue was crystallized from petroleum ether (see table).

Oxidation of 3-acyl-2-(phenylthio)propionitriles to sulfones. To an acetic acid solution of 0.01 mole of the 3-acyl-2-(phenylthio)propionitrile we added 0.06 mole of 28% hydrogen peroxide and a few drops of concentrated sulfuric acid. The precipitate that formed after several days was filtered off and dried in a vacuum desiccator. By the addition of water some more sulfone was isolated from the filtrate. In the case of 3-butyryl-2-(phenylthio)-propionitrile there was no precipitate. The sulfone was isolated by the addition of water to the acetic acid solution. The 3-acyl-2-(phenylsulfonyl)propionitriles were recrystallized from alcohol (see table).

Hydrolysis of 3-benzoyl-2-(phenylthio)propionitrile to the amide. Dropwise addition was made with stirring of 10 ml of 70% perchloric acid to 4 g of 3-benzoyl-2-(phenylthio)propionitrile in 50 ml of glacial acetic acid. The mixture was poured into water, and the precipitate formed was filtered off and dried in a vacuum desiccator; weight 4.05 g; yield 95%; m.p. 155° (from alcohol). Found: C 67.43; H 5.27; N 4.99; S 11.18%. $C_{16}H_{15}O_2NS$. Calculated: C 67.34; H 5.30; N 4.91; S 11.23%.

Hydrolysis of 3-benzoyl-2-(phenylthio)propionamide to 3-benzoyl-2-(phenylthio)propionic acid. To a solution of 1 g (0.0116 mole) of potassium nitrite in 10 ml of water cooled to its freezing point we added, under cooling, 1 g (0.0035 mole) of 3-benzoyl-2-(phenylthio)propionamide in 20 ml of glacial acetic acid and 2 ml of concentrated sulfuric acid. The mixture was warmed gradually to room temperature and then left overnight. On the next day the mixture was heated at 60° until nitrogen ceased to be liberated. The precipitate formed on dilution was filtered off and treated with saturated sodium carbonate solution. Acidification of the sodium carbonate solution with 10% hydrochloric acid gave 0.6 g (60%) of 3-benzoyl-2-(phenylthio)propionic acid, m.p. 133-133.5° (from aqueous alcohol), undepressed by admixture of a known sample prepared by the method in [3].

Elimination of benzenesulfinic acid from 3-benzoyl-2-(phenylsulfonyl)propionitrile. An ethereal solution of 1 g of 3-benzoyl-2-(phenylsulfonyl)propionitrile was shaken with 150 ml of 0.5% NaOH (as five 30 ml portions). The ether layer was washed with water and dried over anhydrous sodium sulfate. After evaporation of the ether we isolated 0.43 g (82%) of 2-cyanovinyl phenyl ketone. The alkaline solution was neutralized with 10% hydrochloric acid, and a solution of 1 g of mercuric chloride in 30 ml of water heated to the boil was added to the hot solution.

The mixture was boiled until a precipitate ceased to separate. The precipitate was filtered off. The phenylmercury chloride separated by extraction with nitromethane could not be purified by the usual methods and was therefore converted into diphenylmercury (m.p. 125°). A mixture melting point test with a known sample [5] showed no depression.

SUMMARY

1. Benzenethiol adds to 2-cyanovinyl ketones in the α-position to the CN group.

2. The resulting 3-acyl-2-(phenylthio)propionitriles can be oxidized to sulfones and hydrolyzed to the corresponding acids.

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REACTIONS OF ALKOXY(CHLOROMETHYL)METHYLSILANES
WITH SODIUM DIETHYL PHOSPHATE AND WITH SODIUM
DIMETHYLPHOSPHINATE

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Reactions leading to the replacement of chlorine in the α-position to a silicon atom in organosilicon compounds by residues of dialkyl phosphates and phosphinic acids have not been studied. The reaction of chloroalkylsilanes with sodium dialkyl phosphites with formation of compounds with an $Si-C-P$ linkage has been described in the literature [1, 2].

In the present work we investigated the replacement of chlorine in alkoxy(chloromethyl)silanes by dialkyl phosphate and phosphinic acid residues. The experiments showed that the chlorine of alkoxy(chloromethyl)silanes reacts with sodium dialkyl phosphates and with sodium dialkylphosphinates with formation of organosilicon compounds containing an $Si-C-O-P$ linkage and containing also functional groups at the silicon atom.

The compounds described were synthesized in accordance with the scheme:

$$1) \quad (CH_3)_n \underset{\underset{CH_2Cl}{|}}{-Si\,(OR)_{3-n}} + NaO-\underset{\underset{O}{\|}}{P}-(CH_3)_2 \xrightarrow{-NaCl} (CH_3)_n-\underset{\underset{\underset{\underset{O}{\|}}{O-P-(CH_3)_2}}{\underset{CH_2}{|}}}{Si-(OR)_{3-n}}$$

$$2) \quad (CH_3)_n \underset{\underset{CH_2Cl}{|}}{-Si\,(OR)_{3-n}} + NaO-\underset{\underset{O}{\|}}{P}-(OC_2H_5)_2 \xrightarrow{-NaCl} (CH_3)_n-\underset{\underset{\underset{\underset{O}{\|}}{O-P-(OC_2H_5)_2}}{\underset{CH_2}{|}}}{Si-(OR)_{3-n}}$$

$$R=C_2H_5; \qquad \underset{\underset{CH_2Cl}{|}}{Si\cdot(CH_3)_2}, \qquad n=1,2$$
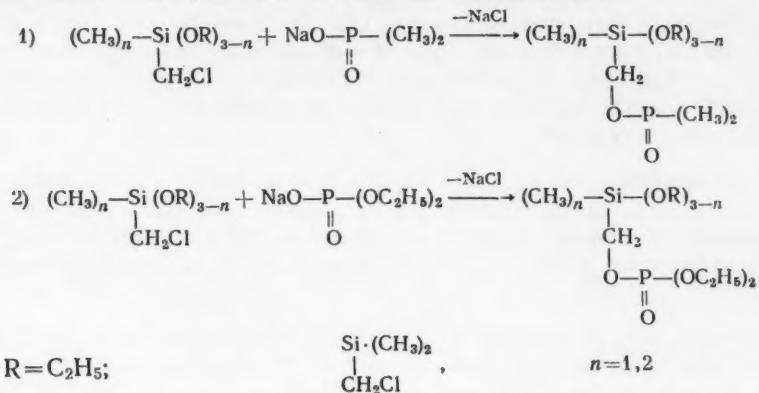
However, judging from the yield of product, sodium dimethylphosphinate reacts the more readily.

As a result of these reactions we obtained new silicon-phosphorus organic compounds, whose properties are given in the table.

EXPERIMENTAL

Sodium diethyl phosphate was prepared by the method of [3] and was dried carefully in a vacuum desiccator over P_2O_5. Sodium dimethylphosphinate was prepared by the usual method by neutralizing dimethylphosphinic acid in an absolute alcohol medium; it was dried in a drying oven at 120-130° for several hours and kept in a vacuum desiccator over P_2O_5.

Synthesis of (diethoxymethylsilyl)methyl dimethylphosphinate (I). The reaction was carried out in a three-necked flask fitted with a stirrer provided with a seal, a reflux condenser protected by a calcium chloride tube, and a thermometer. A mixture of 91.3 g (0.5 mole) of (chloromethyl)diethoxymethylsilane and 58 g (0.5 mole) of sodium dimethylphosphinate was heated with vigorous stirring at 150-160° for 2.5-3 hours. Dry ether was added to the cooled

Substance No.	Formula	B.p. in °C ($\underline{p}$ in mm)	n_D^{20}	d_4^{20}	MR found	MR calculated	Yield (% on amount of silane that reacted)
I	$CH_3-Si-(OC_2H_5)_2$ | $CH_2-O-P(O)(CH_3)_2$	114—115 (2)	1,4325	1,0390	60,02	60,18	80
II	$(CH_3)_2-Si-OC_2H_5$ | $CH_2-O-P(O)(CH_3)_2$	106—108 (4)	1,4355	1,0040	54,74	54,72	50
III	$CH_3-Si-(OC_2H_5)_2$ | $CH_2-O-P(O)(OC_2H_5)_2$	113—115 (1)	1,4182	1,0590	71,52	71,55	35
IV	$(CH_3)_2-Si-OC_2H_5$ | $CH_2-O-P(O)(OC_2H_5)_2$	105—107 (1)	1,4220	1,0400	66,03	66,11	17
V	$(CH_3)_2-Si-O-Si-(CH_3)_2$ | | CH_2 CH_2 | | $O-P(O)(CH_3)_2$ $O-P(O)(CH_3)_2$	208—210 (5)	1,4550	1,0869	86,54	87,06	71

reaction mixture. The precipitate of sodium chloride and unchanged sodium dimethylphosphinate was filtered off and washed repeatedly with dry ether. Ether and unchanged (chloromethyl)diethoxymethylsilane were distilled from the filtrate. The residue was vacuum-fractionated; we isolated 56.7 g (80%)* of a fraction of b.p. 114-115° (2 mm); n_D^{20} 1.4325; d_4^{20} 1.039. Found MR 60.02; calculated MR 60.18. Found: C 39.77; H 8.76; Si 11.73%. $C_8H_{21}O_4SiP$. Calculated: C 39.98; H 8.80; Si 11.65%.

(Ethoxydimethylsilyl)methyl dimethylphosphinate (II). The preparation of (II) was analogous to that of (I). A mixture of 15.3 g (0.1 mole) of (chloromethyl)ethoxydimethylsilane and 11.6 g (0.1 mole) of sodium dimethyl-phosphinate was heated with stirring for six hours at 130°. We obtained 6.7 g (50%) of product; b.p. 106-108° (4 mm); n_D^{20} 1.4355; d_4^{20} 1.0039. Found MR 54.74; calculated MR 54.72. Found: C 39.85; H 9.1; Si 13.34%. $C_7H_{19}O_3SiP$. Calculated: C 39.98; H 9.1; Si 13.36%.

(Diethoxymethylsilyl)methyl diethyl phosphate (III). The synthesis of (III) was analogous to that of (I). By heating 30 g (0.15 mole) of (chloromethyl)diethoxymethylsilane with 16 g (0.091 mole) of sodium diethyl phosphate at 150-160° for six hours we obtained 6.5 g (35%) of product; b.p. 113-115° (1 mm); n_D^{20} 1.4182; d_4^{20} 1.05090. Found MR 71.52; calculated MR 71.55. Found: C 39.65; H 8.58; Si 9.46%. $C_{10}H_{25}O_6SiP$. Calculated: C 39.98; H 8.32; Si 9.35%.

(Ethoxydimethylsilyl)methyl diethyl phosphate (IV). (IV) was prepared similarly to (I) by heating a mixture of 20 g (0.12 mole) of (chloromethyl)ethoxydimethylsilane and 11 g (0.062 mole) of sodium diethyl phosphate at 130° for six hours. We isolated 2 g (17%) of product; b.p. 105-107° (1 mm); n_D^{20} 1.4220; d_4^{20} 1.040. Found MR 66.03; calculated MR 66.11. Found: C 39.42; H 8.62; Si 10.64%. $C_9H_{23}O_5SiP$. Calculated : C 39.98; H 8.57; Si 10.38%.

Oxybis(dimethylsilylene)dimethyl bisdimethylphosphinate (V). The synthesis of (V) was analogous to that of (I). A mixture of 17.6 g (0.075 mole) of 1,3-bischloromethyl-1,1,3,3-tetramethyldisiloxane and 11.6 g (0.1 mole) of sodium dimethylphosphinate was stirred at 160° for 2.5 hours. Vacuum fractionation gave 12.3 g (71%) of product of b.p. 208-210° (5 mm). On standing, the product crystallized out; n_D^{20} 4.4550; d_4^{20} 1.0869. Found MR 86.54; calculated MR 87.06. Found: C 34.70; H 8.20; Si 16.04%. $C_{10}H_{28}O_5Si_2P_2$. Calculated: C 34.67; H 8.14; Si 16.2%.

SUMMARY

The reactions of alkoxy(chloromethyl)methylsilanes with sodium diethyl phosphate and with sodium dimethyl-phosphinate provide a method for the preparation of some silicon-phosphorus organic compounds containing an $Si-C-O-P$ linkage and functional groups attached to the silicon atom.

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* The yields of the products are calculated on the amount of the (chloromethyl)ethoxysilane that reacted.

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TELOMERIZATION OF DIMETHYLCYCLOSILOXANES

COMMUNICATION 1. PREPARATION OF LINEAR α, ω-DICHLOROPOLY-DIMETHYLSILOXANES

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In a previous paper [1] we showed that the reaction of octamethylcyclotetrasiloxane with dichlorodimethylsilane proceeds with the formation of telomers of the polydimethylsiloxane series of the following structure:

$$Cl \left(\begin{array}{c} CH_3 \\ | \\ -Si-O- \\ | \\ CH_3 \end{array} \right)_n \begin{array}{c} CH_3 \\ | \\ Si-Cl \\ | \\ CH_3 \end{array}$$
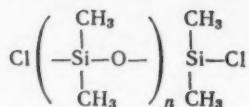
In the present paper we shall describe the telomerization of hexamethylcyclotrisiloxane and of octamethylcyclotetrasiloxane with dichlorodimethylsilane, and also an investigation of the effect of the octamethyltetrasiloxane: dichlorodimethylsilane ratio on the composition of the reaction products.

It was shown that the reactions of dichlorodimethylsilane with hexamethylcyclotrisiloxane and with octamethylcyclotetrasiloxane proceed in accordance with the equation:

$$n\,[(CH_3)_2SiO]_m + (CH_3)_2SiCl_2 \rightarrow Cl\,\{[(CH_3)_2 \cdot SiO)_m\}_n\,Si\,(CH_3)_2Cl$$
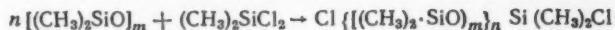
It is probable that the initiation of reaction results from the coordination of one of the oxygen atoms of the methylcyclosiloxane with the silicon atom of dichlorodimethylsilane:
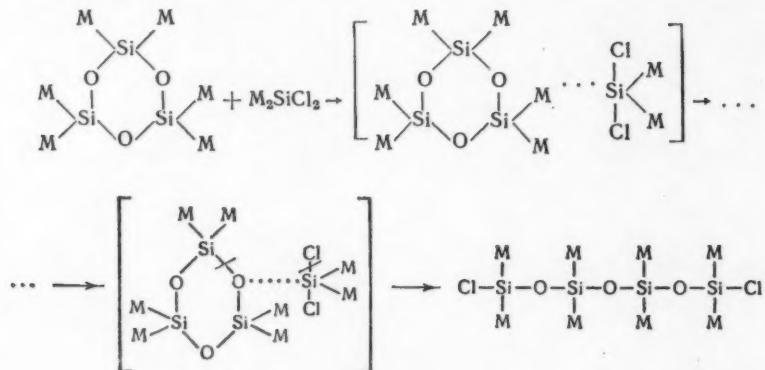
As a result of the weakening of an Si—O bond in the methylcyclosiloxane the conjugated ring is broken with addition of chlorine to a silicon atom and of chlorodimethylsilyl to oxygen.

The further process of chain growth is probably associated with the coordination of terminal silicon atoms with oxygen of the cyclic substance with subsequent opening of the ring and formation of a linear α,ω-dichloropolydimethylsiloxane by the reactions:

TABLE 1

Formula	Physical properties					Given analysis, %									
	B.p. in °C (p in mm)		d_4^{20}		n_D^{20}	MR		Cl		Si		C		H	
	found	literature data	found	literature data	found	calc.	found	calc.	found	calc.	found	calc.	found	calc.	found
Cl[(CH₃)₂SiO]₃(CH₃)₂SiCl	111 (20)	111 (20) [2]	1,011	1,010 [2]	1,4027	—	—	20,02	20,11 20,05	32,96	33,30 33,36	Not analyzed			
Cl[(CH₃)₂SiO]₄(CH₃)₂SiCl	139 (20)	138 (20)	1,0048	—	1,4032	102,68	103,22	16,68	16,58 16,43	34,21	31,20 33,93	28,21	28,67 28,67	7,1	7,00 7,09
Cl[(CH₃)₂SiO]₆(CH₃)₂SiCl	181—184 (21)	—	0,9996	—	1,4035	141,67	140,81	12,37	12,19 11,82	34,97	34,96 35,24	29,29	29,50 29,49	7,37	7,74 7,76
Cl[(CH₃)₂SiO]₈(CH₃)₂SiCl	218 (20)	—	0,9945	—	1,4042	179,06	178,56	9,83	9,45	35,23	35,26 25,92	29,93	29,82 29,66	7,53	7,38 7,26
Cl[(CH₃)₂SiO]₉(CH₃)₂SiCl	231—233 (20)	—	0,9927	—	1,4048	197,76	196,92	8,91	8,40 8,97	35,80	35,90 35,95	30,15	30,28 30,25	7,59	7,87 7,58
Cl[(CH₃)₂SiO]₁₂(CH₃)₂SiCl	246—248 (8)	—	0,9885	—	1,4060	253,85	253,13	6,96	6,96 6,86			30,65	30,54 30,64	7,71	7,65 7,62
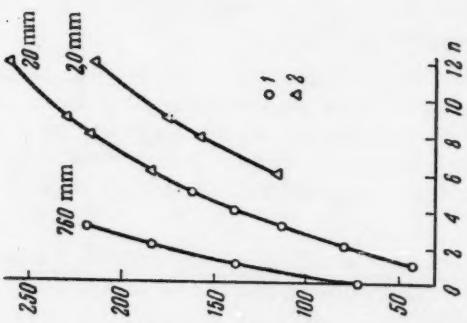
Fig. 1. Relation of boiling point to the number of silicon atoms in the molecule of Cl[(CH₃)₂SiO]ₙ(CH₃)₂SiCl: 1) Data in literature; 2) experimental results.
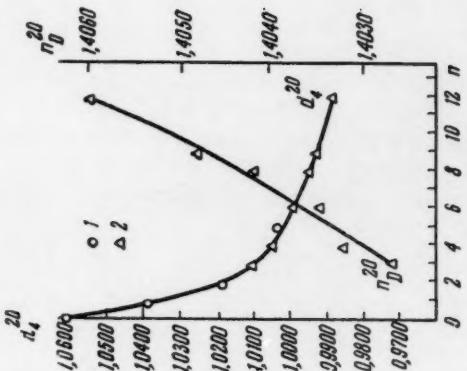
Fig. 2. Relation of specific gravity and of refractive index to the number of silicon atoms in the molecule of Cl[(CH₃)₂SiO]ₙ(CH₃)₂SiCl: 1) Data in literature; 2) experimental results.
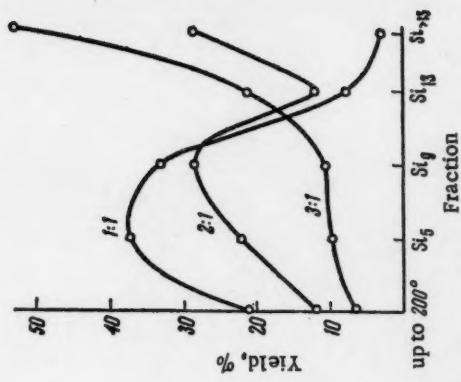
Fig. 3. Effect of octamethylcyclotetrasiloxane : dichlorodimethylsilane ratio on the yield of telomers.

$$\text{(hexamethylcyclotrisiloxane ring)} + M-\underset{\underset{M}{|}}{\overset{\overset{Cl}{|}}{Si}}-\left[\left(O-\underset{\underset{M}{|}}{\overset{\overset{M}{|}}{Si}}\right)_3\right]_n Cl \longrightarrow$$

$$\longrightarrow \left[\text{(ring)}\cdots\cdots\underset{\underset{M\ M}{|}}{\overset{\overset{Cl}{|}}{Si}}-\left[\left(O-\underset{\underset{M}{|}}{\overset{\overset{M}{|}}{Si}}\right)_3\right]_n Cl\right] \longrightarrow$$

$$\longrightarrow Cl-\underset{\underset{M}{|}}{\overset{\overset{M}{|}}{Si}}-\left[\left(O\underset{\underset{M}{|}}{\overset{\overset{M}{|}}{Si}}\right)_3\right]_{n+1} Cl$$
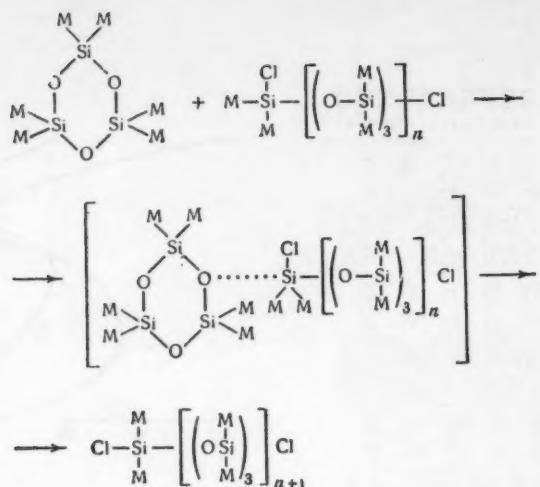
When this reaction is carried out between equimolecular amounts of hexamethylcyclotrisiloxane and dichlorodimethylsilane at 250° for three hours, telomers of general formula (I)

$$Cl\left[\left(\underset{\underset{M}{|}}{\overset{\overset{M}{|}}{Si}}O\right)_3\right]_n \underset{\underset{M}{|}}{\overset{\overset{M}{|}}{Si}}-Cl$$
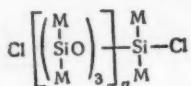
are formed in the following amounts: 38.5% of the telomer with $n = 1$; 24.1% of the telomer with $n = 2$; 4.47% of the telomer with $n = 3$; 0.63% of the telomer with $n = 4$. Under the same conditions the reaction between octamethylcyclotetrasiloxane and dichlorodimethylsilane leads to the formation of products of general formula (II)

$$Cl\left[\left(\underset{\underset{M}{|}}{\overset{\overset{M}{|}}{Si}}O\right)_4\right]_n \underset{\underset{M}{|}}{\overset{\overset{M}{|}}{Si}}Cl$$
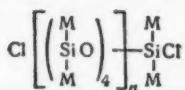
in yields of 38.86% for $n = 1$, 32.95% for $n = 2$, and 7.47% for $n = 3$. The properties of telomers of general formulas (I) and (II), and also data of their analysis, are given in Table 1.

An investigation of the relation of the properties of members of the homologous series of α,ω-dichloropolydimethylsiloxanes to the number of silicon atoms in the molecule showed that the boiling point (Fig. 1), and also the specific gravity and refractive index (Fig. 2), changes in a regular way and no anomalies are observed. This makes it possible to utilize the data obtained to determine the properties of other members of the α,ω-dichloropolydimethylsiloxane series.

The telomerization of octamethylcyclotetrasiloxane with dichlorodimethylsilane was studied for different molar proportions of the components; in particular the ratios 1 : 1, 2 : 1, and 3 : 1 were studied. The experiments showed (Fig. 3) that at none of the ratios studied does telomerization lead to individual products; it gives a mixture of telomers with a maximum yield of the product corresponding to the given ratio. Increase in the ratio of the reactants leads to a reduction in the yield of low telomers and a sharp increase in the amount of high-boiling products.

EXPERIMENTAL

Reaction of hexamethylcyclotrisiloxane with dichlorodimethylsilane. For the syntheses we used crystalline hexamethylcyclotrisiloxane (m.p. 62-64°; b.p. 132-136°; mol. wt. 222.45) and dichlorodimethylsilane of chlorine content 55.7% (mol. wt. 129.08). A dry 500-ml stainless steel autoclave was charged with a mixture of 222.5 g (1.0 mole) of hexamethylcyclotrisiloxane and 129.1 g (1.0 mole) of dichlorodimethylsilane. The apparatus was warmed up to 250° in the course of one hour and was kept at this temperature for three hours. When the apparatus was cool, 345 g of product was discharged, and this was then fractionated from a flask with a 20 mm column. The

TABLE 2

Fraction	Pressure (mm)	B.p. of fraction (°C)	Yield (g)	Found Cl. %	Si_4 Cl % calc.=20,02	Si_7 Cl % calc.=12,37	Si_{10} Cl % calc.=8,93	Si_{13} Cl % calc.=6,96
					Content of product (g)			
I	760	До 100	7,9	—	—	—	—	—
II	760	100—155	33,9	—	—	—	—	—
III	760	155—185	10,2	—	—	—	—	—
IV	760	185—200	30,2	21,26	30,2	—	—	—
V	20	До 100	22,0	21,78	22,0	—	—	—
VI	20	110—120	29,1	20,17	29,1	—	—	—
VII	20	120—150	63,0	17,5	38,5	24,5	—	—
VIII	20	150—175	35,0	15,13	12,75	22,25	—	—
IX	20	175—187	15,7	12,62	—	15,7	—	—
X	20	187—220	29,8	11,31	—	20,5	9,3	—
XI	20	220—235	6,1	8,78			6,1	
XII	2	210—235	2,13	7,19	—	—	—	2,13
		Residue	24,67	—				
Total (g)			340,1	—	132,55	82,95	15,4	2,13
%			100		38,5	24,1	4,47	0,63

TABLE 3. Ratio 1 : 1; Charge in Autoclave: Octamethylcyclotetrasiloxane 148.3 g (0.5 mole) and Dichlorodimethylsilane 64.54 g (0.5 mole); Charge in Still 212.5 g.

Fraction	Pressure (mm)	B.p. of fraction (°C)	Yield (g)	Found Cl. %	Si_4 Cl % calc.=16,7%	Si_9 Cl calc. = 9,85%	Si_{13} Cl calc.= 6,96%
					Content of product (g)		
I	760	До 200	41,52	—	—	—	—
II	20	» 125	38,76	19,19	36,3	2,52	
III	20	125—155	28,82	16,63	26,3	11,0	
IV	4	До 125	21,0	3,13	10,0	10,83	
V	4	125—155	15,6	11,94	4,77	41,0	
VI	4	155—200	48,44	9,45	—	3,77	
VII	4	200—230	12,1	7,86			7,44
VIII		Residue	6,7				8,33
Total (g)			212,39		77,37	69,12	15,77
%			100		36,86	32,95	7,97

TABLE 4. Ratio 2 : 1; Charge in Autoclave: Octamethylcyclotetrasiloxane 258 g (0.87 mole) and Dichlorodimethylsilane 55.7 g (0.435 mole); Charge in Still 293 g

Fraction	Pressure (mm)	B.p. of fraction (°C)	Yield (g)	Found Cl. %	Si_4 Cl calc. =16,7 %	Si_9 Cl calc.=9,85 %	Si_{13} Cl calc.= 6,96 %
					Content of product (g)		
I	760	До 200	32,9	—	—	—	—
II	760	210—240	49,4	16,48	49,4	—	—
III	8	130—140	6,0	13,95	3,6	2,4	—
IV	8	140—155	16,0	12,65	6,0	10,0	—
V	8	155—170	9,4	11,39	2,15	7,25	—
VI	8	170—210	58,0	9,69	—	58,0	—
VII	8	210—220	8,9	8,27	—	4,13	4,77
VIII	8	220—230	9,2	7,41	—	1,5	7,7
IX	8	230—260	22,6	6,81	—	—	22,6
X	8	Residue	75,1	—			
Total (g)			288,51	—	61,15	84,28	35,07
%			100		22,0	28,5	11,9

TABLE 5. Ratio 3 : 1; Charge in Autoclave: Octamethylcyclotetrasiloxane 267 g (0.9 mole) and Dichlorodimethylsilane 38.7 g (0.3 mole); Charge in Still 299.4 g

Fraction	Pressure (mm)	B.p. of fraction (°C)	Yield (g)	found Cl, %	Content of product (g)		
					Si_4 Cl calc.=16,7 %	Si_6 Cl calc.=9,65 %	Si_{13} Cl calc.=6,96 %
I	760	До 200	29,63	—	—	—	—
II	2	До 130	26,80	16,44	26,8		
III	2	130—160	20,12	9,48	—	20,12	
IV	2	160—209	22,55	8,27	—	10,18	12,37
V	2	209—235	46,37	7,05	—	—	46,37
VI			151,07	—			
Total (g)			286,64		26,8	30,30	58,74
%			100		9,4	9,4	20,8

chlorine contents were determined by titration on all the fractions collected. From the chlorine contents found the contents of pure products in the fractions were calculated on the assumption that intermediate fractions were mixtures of the two relevant pure products. The fractionation results, the chlorine contents, and the calculated contents of pure products in the fractions are given in Table 2.

By two distillations we isolated the corresponding pure products from Fractions IV, V, VI, IX, XI, and XII: $Cl[(CH_3)_2SiO]_3(CH_3)_2SiCl$, $Cl[(CH_3)_2SiO]_6(CH_3)_2SiCl$, $Cl[(CH_3)_2SiO]_9(CH_3)_2SiCl$, $Cl[(CH_3)_2SiO]_{12} \cdot (CH_3)_2SiCl$; the properties of these and the analytical figures are given in Table 1.

Reactions of octamethylcyclotetrasiloxane with dichlorodimethylsilane. For the syntheses we used octamethyl-cyclotetrasiloxane of b.p. 174-176° (mol. wt. 296.6) and dichlorodimethylsilane of chlorine content 55.7% (mol. wt. 129.08). The reaction, the fractionation of the products, and the calculation of contents of pure substances were carried out as described above. The experimental data on the charging of the apparatus, and also results of the fractionations, chlorine contents, and the calculations of the contents of pure substances in the fractions, are given for the ratios 1 : 1, 2 : 1, and 3 : 1 in Tables 3, 4, and 5 respectively. From fractions II, VI, and IX (Table 4) by two distillations we isolated, respectively, the pure products: $Cl[(CH_3)_2SiO]_4 \cdot (CH_3)_2SiCl$, $Cl[(CH_3)_2SiO]_8(CH_3)_2SiCl$, $Cl[(CH_3)_2SiO]_{12}(CH_3)_2SiCl$; the properties of these and the analytical figures are given in Table 1.

SUMMARY

1. The telomerization of dimethylcyclosiloxanes with dichlorodimethylsilane was discovered: it leads to the formation of polymer-homologs containing inorganic chains, namely α,ω-dichloropolydimethylsiloxanes of the general formula:

$$Cl \left(\begin{array}{c} CH_3 \\ | \\ -SiO- \\ | \\ CH_3 \end{array} \right)_n \begin{array}{c} CH_3 \\ | \\ -Si-Cl \\ | \\ CH_3 \end{array}$$
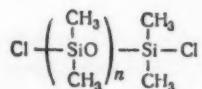
2. α,ω-Dichloropolydimethylsiloxanes were isolated containing 4, 5, 7, 9, 10, and 13 silicon atoms in the molecule, and their properties were studied.

3. A mechanism is proposed for the telomerization of inorganic cycles "framed" with methyl groups.

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2. W. Patnode and D. Wilcock, J. Am. Chem. Soc. 68, 2291 (1946).

PERFLUORO α,ω-DIOLEFINS AND SOME OF THEIR REACTIONS

I. L. Knunyants, Li Dzhi-yuan', and V. V. Shokina

The telomerization reaction, which has been applied extensively in recent years, opens up wide possibilities for the preparation of polyfluoro hydrocarbons of high molecular weight and their various derivatives, differing in the terminal groups of the telomer. Numerous different telomers of fluoro olefins have now been prepared. In 1951 Haszeldine [1] reported the telomerization of tetrafluoroethylene with iodine with formation of polyfluoro-α,ω-diiodoalkanes of general formula $I(CF_2CF_2)_nI$ in which $\underline{n}$ = 4-18, but the author does not give the experimental conditions. Our experiments in this direction gave very low yields of a mixture of telomers. Moreover, the inability of the CF_2I group to undergo heterolytic reactions greatly limits the possibility of passing from diiodo compounds to derivatives of other types. In the thermal telomerization of tetrafluoroethylene with 1,2-dichlorotrifluoroiodoethane Hauptschein and others [2] obtained only a solid product which did not contain iodine and was probably polyfluoro-ethylene.

By the telomerization of tetrafluoroethylene with 1,2-dichlorotrifluoroiodoethane in presence of benzoyl per-oxide as initiator we succeeded in obtaining, in good yields, the lower telomer-homologs and the higher telomers, which were waxlike substances $CF_2Cl \cdot CFClI + nCF_2 = CF_2 \rightarrow CF_2ClCFCl(CF_2CF_2)_nI$ in which $\underline{n}$ = 1, 2, 3, and 4 (Tables 1 and 2). As in all cases of telomerization the proportions of the telomers in the reaction products depends on the reaction conditions and the amount of telogen used. In all experiments the amount of benzoyl peroxide was 1% on the weight of dichlorotrifluoroiodoethane taken for reaction.

By the action of zinc on solutions of telomers in methylene chloride in presence of acetic anhydride [3] we obtained α,β,ψ,ω-tetrachloropolyfluoroalkanes (Table 3), which by dechlorination with zinc in acetic acid were converted into perfluoro α,ω-dienes (Table 4).

$$2CF_2ClCFCl(CF_2CF_2)_n I \xrightarrow{CH_2Cl_2} CF_2ClCFCl(CF_2CF_2)_{2n}CFClCF_2Cl$$

$$Zn \Big| \text{ in } CH_3COOH$$

$$CF_2=CF(CF_2CF_2)_{2n}CF=CF_2$$
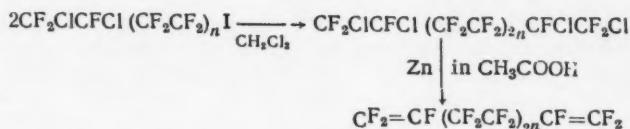
In this way we obtained perfluoro-1,7-octadiene, perfluoro-1,11-dodecadiene, and perfluoro-1,15-hexadecadiene. Moreover, by coupling together a mixture of different telomers we obtained tetrachloro compounds from which we isolated 1,2,5,6-tetrachlorodecafluorohexane and 1,2,9,10-tetrachlorooctadecafluorodecane (see Table 3).

$$CF_2ClCFClJ + CF_2ClCFClCF_2CF_2J \xrightarrow{\underset{CH_2Cl_2}{Zn}}$$

$CF_2ClCFClCFClCF_2Cl$ 21,1%
$CF_2ClCFClCF_2CF_2CFClCF_2Cl$ 24,3%
$CF_2ClCFCl(CF_2CF_2)_2CFClCF_2Cl$ 22,1%

$$CF_2ClCFClCF_2CF_2J + CF_2ClCFCl(CF_2CF_2)_2J \xrightarrow{\underset{CH_2Cl_2}{Zn}}$$

$CF_2ClCFCl(CF_2CF_2)_2CFClCF_2Cl$ 20,0%
$CF_2ClCFCl(CF_2CF_2)_3CFClCF_2Cl$ 38,2%
$CF_2ClCFCl(CF_2CF_2)_4CFClCF_2Cl$ 23,7%

By the dechlorination of 1,2,9,10-tetrachlorooctadecafluorodecane we obtained perfluoro-1,9-decadiene (see Table 4).

TABLE 1. Reaction Conditions and Yields of Telomer-Homologs

Ratio of $CF_2ClCFClI$ to $CF_2=CF_2$	Reaction temp. (°C)	Reaction time (hr)	Yield of telomers (%*)		
			$n=1$	$n=2$	$n \geqslant 3$
2 : 1	135	4	62,4	19,8	—
1 : 1	130	5	57,0	24,0	4,5
1 : 2	130	4	39,2	23,0	25

* On the 1,2-dichlorotrifluoroiodoethane that reacted. The benzoyl peroxide bringing about the radical telomerization was converted to a considerable extent into iodobenzene.

TABLE 2

n	B.p. in °C ($\underline{p}$ in mm)	M.p. (°C)	d_4^{20}	n_D^{20}	MR found	MR calc.	M found	M calc.	Found (%) C	Found (%) F	Calc. (%) C	Calc. (%) F
1	66 (67)	—	2,135	1,4046	43,47	44,18	374	379	12,44	36,21	12,68	35,11
2	83 (35)	—	2,095	1,3840	53,34	53,98	479,5	479	14,72	43,28	15,05	43,64
			d_4^{30}	n_D^{30}								
3	82 (3)	22—24	2,078	1,3710	63,17	63,76	569	579	16,69	49,11	16,58	49,22
4	110—111 (7)	70—71	—	—	—	—	—	—	17,99	52,67	17,67	53,17

TABLE 3

n	Yield (%)	B.p. in °C ($\underline{p}$ in mm)	M.p. (°C)	d_4^{20}	n_D^{20}	MR found	MR calc.	Found (%) C	Found (%) F	Calc. (%) C	Calc. (%) F
1	24,3	80 (34)	—	1,7215	1,3704	49,84	50,76	18,08	46,84	17,82	47,01
2	80	67 (3)		1,838	1,3604	60,58	60,56	18,89	53,22	19,06	52,79
				d_4^{35}	n_D^{35}						
3	38,2	94 (5)	29—30	1,858	1,3496	69,88	70,34	19,80	57,56	19,86	56,62
4	77	116 (5)	68					20,82	59,33	20,46	59,37
6	91,5		126—128					21,18	63,63	21,05	63,05
8	85		160					21,52	66,01	21,74	65,40

By oxidation with potassium permanganate in aqueous-acetone solution, all the perfluoro α,ω-diolefins obtained were converted in good yield into the corresponding perfluoro dicarboxylic acids $HOOC(CF_2CF_2)_nCOOH$, in which $\underline{n}$ = 2, 3, 4, and 6 (Table 5).

Until now only a few fluorinated dicarboxylic acids have been obtained in very low yields by the electrochemical fluorination of the corresponding dicarboxylic acids [4] or by the oxidation of unsaturated fluoro hydrocarbons [5, 6]. From perfluorodipic and perfluorosebacic acids acid chlorides were prepared for the first time by the action of thionyl chlorine in presence of catalytic amounts of KCl or KOH, and from these dianilides and diamides were prepared. The use of KCl as catalyst in the preparation of the acid chlorides of strong acids was reported earlier by Kraft and co-workers [7]. By the polycondensation of perfluoroadipoyl and of perfluorosebacoyl chlorides with 1,6-hexanediamine at the interface of two media (water—CCl_4), fluorinated polyamides have been prepared.

TABLE 4

n	Perfluoro diolefins	Yield (%)	B.p. (°C)	d_4^{20}	n_D^{20}	MR found	MR calc.	Found (%) C	Found (%) F	Calc. (%) C	Calc. (%) F
2	Perfluoro-1,7-octadiene	72,5	106	1,695	1,3020	40,52	40,18	26,72	73,24	26,54	73,47
3	Perfluoro-1,9-decadiene	67,8	148	1,796	1,3100	49,56	43,98	25,97	74,55	25,97	74,03
4	Perfluoro-1,11-dodecadiene	60	181—182	1,826	1,3315	59,99	59,78	25,60	74,38	25,62	74,38
6	Perfluoro-1,15-hexadecadiene	72,9	147—149 (33 mm) M.p. 73—74	—	—	—	—	25,31	74,45	25,20	74,80

TABLE 5

n	Acid	Yield,%	M.p. (°C)	Neutralization equivalent Found	Neutralization equivalent calc.	Found, % C	Found, % H	Found, % F	Calculated, % C	Calculated, % H	Calculated, % F	Literature ref.
2	Perfluoroadipic	86	134—135	144,5	145,0	24,88	0,75	52,42	24,83	0,69	52,41	[2]
3	Perfluorosuberic	95	143—144	198	195	24,52	0,46	—	24,62	0,51	58,46	
4	Perfluorosebacic	92	160—161*	244	245	24,83	0,49	62,13	24,50	0,41	62,04	[1]
6	Perfluorotetradecanedioic	71,8	191—193**	337	345	24,66	0,37	—	24,36	0,29	66,09	

* From water.
** From dioxane.

Telomerization of tetrafluoroethylene with 1,2-dichlorotrifluoroiodoethane. A 250 ml rotating steel autoclave was charged with 200 g (0.72 mole) of dichlorotrifluoroiodoethane and 2 g of freshly precipitated benzoyl peroxide. The autoclave was purged with dry nitrogen, cooled to –60°, and evacuated; 14 liters (0.7 mole) of tetrafluoroethylene was then condensed in the autoclave, which was heated with shaking for four hours at 130°. When the autoclave, which was heated with shaking for four hours at 130°. When the autoclave was cool, unchanged tetrafluoroethylene was transferred from the autoclave to a gas holder (5 liters), and the reaction mixture was distilled through a column of 17-plate efficiency. We collected the following fractions: 1) Unchanged dichlorotrifluoroiodoethane, 108 g, b.p. 53° (150 mm) and 99-102° (760 mm). 2) 1,2-Dichloroheptafluoro-4-iodobutane, 72 g (57% on the dichlorotrifluoroiodoethane that reacted); b.p. 66° (67 mm); n_D^{20} 1.4046; d_4^{20} 2.135. Found MR 43.47; M 374; calculated MR $C_4F_7Cl_2I$ MR 44.18; M 379. Found: C 12.44, 12.68; F 36.21, 35.69%. Calculated: C 12.68; F 35.11%. 3) A mixture of iodobenzene and 1,2-dichloroundecafluoro-6-iodohexane, b.p. 81° (35 mm). 4) 1,2-Dichloroundecafluoro-6-iodohexane, 37.5 g (24% on the dichlorotrifluoroiodoethane that reacted); b.p. 83-84° (35 mm); n_D^{20} 1.3830; d_4^{20} 2.095. Found MR 53.34; M 479.5; calculated MR $C_6F_{11}Cl_2I$

TABLE 6. Fractionation Results

Fraction	B.p. (°C)	Wt. (g)	Yield (%)	Formula
I	до 133	6		
II	133—135	40,1	22,1	$C_4F_6Cl_4$
III	135—170	7,5		
IV	170—172	58,8	24,3	$C_6F_{10}Cl_4$
V	172—201	9,0		
VI	75—76 (4mm)	67,0	22,1	$C_8F_{14}Cl_4$
Residue		2,0		

MR 53.98, M 479. Found: C 14.49, 14.72; F 44.07, 43.28%. $C_6F_{11}Cl_2I$. Calculated: C 15.05; F 43.64%.

The residue was 5 g of a thick crystallizing mass (mixture of higher telomers).

Under the same conditions from 93 g (0.33 mole) of 1,2-dichlorotrifluoroiodoethane, 1 g of benzoyl peroxide, and 14 liters (0.7 mole) of tetrafluoroethylene we obtained: 1) Unchanged dichlorotrifluoroiodoethane, 53 g. 2) 1,2-Dichloroheptafluoro-4-iodobutane, 21 g (39% on the dichlorotrifluoroiodoethane that reacted). 3) 1,2-Dichloroundecafluoro-6-iodohexane, 15.8 g (23%). 4) 1,2-Dichloropentadecafluoro-8-iodooctane, 20 g (24%); b. p. 82° (3 mm); m.p. 22-24°; n_D^{30} 1.3710; d_4^{30} 2.078. Found M 569; MR 63.17; calculated MR $C_8F_{15}Cl_2I$ M 579; MR 63.76. Found: C 16.69; F 49.11%. Calculated: C 16.58; F 49.22%.

For the mixture of higher telomers by fractionation through a column we isolated 1,2-dichlorononadecafluoro-10-iododecane; b.p. 110-111° (7 mm); m.p. 70-71°. Found: C 17.99; F 52.67%. $C_{10}F_{19}Cl_2I$. Calculated: C 17.67; F 53.17%.

1,2,7,8-Tetrachlorotetradecafluorooctane. Gradual addition was made of 56.9 g (0.15 mole) of 1,2-dichloroheptafluoro-4-iodobutane to a stirred mixture of 10.0 g (0.15 mole) of granulated zinc, 31.0 g (0.3 mole) of acetic anhydride, and 50 ml of dry methylene chloride. Spontaneous evolution of heat occurred. Addition of the iodo compound was regulated in such a way that the temperature of the reaction mixture remained about 40°. When the addition was complete, the reaction mixture was stirred for six hours at 40°, after which 100 ml of water was added with cooling and stirring; the lower layer was separated, washed with water, dried with magnesium sulfate, and distilled through a column. We obtained 29.9 g (80%) of 1,2,7,8-tetrachlorotetradecafluorooctane; b.p. 67-68° (3 mm); n_D^{20} 1.3604; d_4^{20} 1.838. Found MR 60.58; M 505; calculated MR $C_8F_{14}Cl_4$ MR 60.56; M 504.00. Found: C 18.89; F 53.22%. Calculated: C 19.06; F 52.79%.

1,2,11,12-Tetrachlorodocosafluorododecane. Gradual addition was made of 96 g (0.2 mole) of 1,2-dichloroundecafluoro-6-iodohexane in 50 ml of methylene chloride to a stirred mixture of 13.5 g (0.2 mole) of granulated zinc, 41 g (0.4 mole) of acetic anhydride, and 150 ml of dry methylene chloride. The reaction conditions were as described for the preceding experiment. The reaction product was filtered off together with zinc, dried, and distilled. We obtained 54 g (77%) of 1,2,11,12-tetrachlorodocosafluorododecane; b.p. 68-68.5° (from CCl_4). Found: C 20.82; F 59.33%. $C_{12}F_{22}Cl_4$. Calculated: C 20.46; F 59.37%.

1,2,15,16-Tetrachlorotriacontafluorohexadecane. Gradual addition was made of 126 g (0.216 mole) of 1,2-dichloropentadecafluoro-8-iodooctane in 50 ml of methylene chloride to a stirred mixture of 26 g (0.4 mole) of granulated zinc, 40 g of acetic anhydride, and 220 ml of dry methylene chloride. When the addition of the iodo compound was complete, the reaction mixture was stirred for nine hours at 40°; 250 ml of water was then added with cooling. The insoluble white precipitate was filtered off together with zinc, washed with water, and dried

in air. The product was extracted with hot carbon tetrachloride. The carbon tetrachloride was distilled off and we obtained 90 g (91.5%) of 1,2,15,16-tetrachlorotriacontafluorohexadecane, m.p. 126-128° (from CCl₄). Found: C 21.18; F 63.63%. $C_{16}F_{30}Cl_4$. Calculated: C 21.05; F 63.05%.

1,2,19,20-Tetrachlorooctatriacontafluoroeicosane. Under the same conditions from 1,2-dichlorononadecafluoro-10-iododecane we obtained an 86% yield of 1,2,19,20-tetrachlorooctatriacontafluoroeicosane, b.p. 206-210° (8 mm) and m.p. 160-161° (from CCl₄). Found: C 21.52; F 66.01. $C_{20}F_{38}Cl_4$. Calculated: C 21.74; F 65.40%.

1,2,5,6-Tetrachlorodecafluorohexane. A mixture of 168 g (0.6 mole) of 1,2-dichlorotrifluoroiodoethane and 228 g (0.6 mole) of 1,2-dichloroheptafluoro-4-iodobutane was added gradually with stirring to a mixture of 120 g of granulated zinc, 240 ml of acetic anhydride, and 500 ml of dry methylene chloride. When the addition of the iodo compounds was complete, the reaction mixture was stirred for nine hours at 40°, after which 300 ml of water was added with cooling and stirring the layer was separated, and to complete the hydrolysis of the acetic anhydride it was added with stirring to 200 ml of boiling 5% sulfuric acid. The reaction mixture was stirred further with heating for one hour. The lower layer was separated, washed, first with water, then with sodium bicarbonate solution, and then again with water, and dried over magnesium sulfate. Fractionation through a column gave 58.8 g of 1,2,5,6-tetrachlorodecafluorohexane (Table 6).

TABLE 7. Fractionation Results

Fraction	B.p. in °C (p in mm)	Wt. (g)	Yield (%)	Formula
I	(8 (5)	60,5	20,0	$C_8F_{14}Cl_4$
II	69—93 (5)	8,0		
III	94 (5)	138,3	38,2	$C_{10}F_{18}Cl_4$
IV	96—110 (5)	6,5		
Residue		100,0	23,7	$C_{12}F_{22}Cl_4$

Constants of 1,2,5,6-tetrachlorodecafluorohexane: b.p. 170.5°; 80° (34 mm); n_D^{20} 1.3704; d_4^{20} 1.7215. Found MR 49.84; MR calculated MR $C_6F_{10}Cl_4$ 50.76. Found: C 18.02; F 46.84%. Calculated: C 17.82; F 47.01%.

1,2,9,10-Tetrachlorooctadecafluorodecane. Under the same conditions from 228 g (0.6 mole) of 1,2-dichloroheptafluoro-4-iodobutane and 288 g (0.6 mole) of 1,2-dichloroundecafluoro-6-iodohexane we obtained 1,2,9,10-tetrachlorooctadecafluorodecane in 38.2% yield. The results of the experiment are shown in Table 7.

Constants of 1,2,9,10-tetrachlorooctadecafluorodecane; b.p. 94° (5 mm); m.p. 29-30°; n_D^{35} 1.3496; d_4^{35} 1.858. Found MR 69.88; calculated MR 70.34. Found: C 19.80; F 57.56%. $C_{10}F_{18}Cl_4$. Calculated: C 19.85; F 56.62%.

Perfluoro α,ω-diolefins. Gradual addition was made of 0.1 mole of the $\alpha, \beta, \psi, \omega$-tetrachloroalkane (fully fluorinated) to a mixture of 180 ml of acetic acid, 60 ml of acetic anhydride, and 40 g of granulated zinc at 118° with stirring. The reaction mixture was heated at the boiling point for 12 hours, cooled, and diluted with water. The lower layer was separated, washed, first with water, then with sodium bicarbonate solution, and finally again with water, dried over magnesium sulfate, and distilled through a column. In the preparation of perfluoro-1,7-octadiene the boiling point of the reaction mixture gradually fell to 103-107°, and the reaction product was distilled off. The distillate was washed in the usual way and fractionated through a column. In the preparation of perfluoro-1,15-hexadecadiene, after dilution of the reaction mixture with water the reaction product was extracted with trichlorotrifluoroethane (Freon 113). The Freon was distilled off, and then the perfluoro-1,15-hexadecadiene. The residues remaining after the distillation of the olefins were treated again with zinc and acetic acid, and further amounts of perfluoro diolefins were obtained. The yield and properties of the perfluoro diolefins are given in Table 4.

Perfluoro dicarboxylic acid. A three-necked flask fitted with stirrer, dropping funnel, and thermometer was charged with 75 ml of water, 75 ml of chemically pure acetone, and 19 g (0.12 mole) of potassium permanganate. A solution of 0.03 mole of the perfluoro diolefin in acetone was added dropwise to the mixture with stirring at 15-20°. Stirring was continued for five hours. The reaction mixture was left overnight. The precipitate was filtered off and washed with hot water. The solution was decolorized with sulfur dioxide and acidified with 50% sulfuric acid. Water and acetone were vacuum-distilled off down to a volume of 70 ml. The residue was extracted with ether in an extractor for five hours. The ether extract was dried over magnesium sulfate, and ether was vacuum-distilled off. The residue was recrystallized from toluene and dried in an Abderhalden pistol over P_2O_5 at 100°. In the preparation of perfluorotetradecanedioic acid 2 g of the diolefin was dissolved in 100 ml of acetone and the reaction was carried out at 40-50°. Because of the low solubility of both the acid itself and its potassium salt in water, at the end of the reaction the mixture was not filtered, but sulfur dioxide was passed through it until the MnO_2 had dissolved completely. Water and acetone were distilled off until the volume was 70 ml, and the mixture was acidified with sulfuric acid to Congo red; the acid was extracted with ether. The results of the experiments are given in Table 5.

Perfluoroadipoyl chloride. A mixture of 3.4 g (0.0117 mole) of perfluoroadipic acid, 5 ml of thionyl chloride, and 0.05 g of potassium hydroxide was placed in a flask fitted with reflux condenser. The mixture was heated in a water bath for eight hours and then distilled. We obtained 3.0 g (78.3%) of perfluoroadipoyl chloride; b.p. 131-132°; n_D^{20} 1.3488; d_4^{20} 1.679. Found MR 41.70; calculated MR 40.77. Found MR 84.1; calculated MR 81.8. Found: C 21.90; F 46.83; Cl 12.50%. $C_6H_8Cl_2O_2$. Calculated: C 21.38; F 46.48; Cl 13.46%.

Dianilide of perfluoroadipic acid. M.p. 196-196.5° (from ethanol). Found: C 49.10; H 2.72; F 35.15%. $C_{18}H_{12}F_8N_2O_2$. Calculated: C 49.09; H 2.73; F 34.54%.

Perfluorosebacoyl chloride. By the same method we prepared perfluorosebacoyl chloride; b.p. 101-103° (23 mm); m.p. 29-30°; yield 80%; n_D^{37} 1.3336; d_4^{37} 1.771. Found MR 61.30; calculated MR 60.38. Found MR 130.0; calculated MR 131.8. Found: C 22.75; F 57.76; Cl 12.50%. $C_{10}F_{16}Cl_2O_2$. Calculated: C 22.77; F 57.68; Cl 13.47%.

Dianilide of perfluorosebacic acid. M.p. 199.5-200° (from ethanol). Found: C 41.30; H 1.86; F 47.33%. $C_{22}H_{12}F_{16}N_2O_2$. Calculated: C 41.25; H 1.88; F 47.50%.

Diamide of perfluorosebacic acid. M.p. 239-241° (from acetic acid). Found: C 24.76; H 0.68; F 61.13%. $C_{10}H_4F_{16}N_2O_2$. Calculated: C 24.59; H 0.83; F 62.30%.

Polyamide from perfluoroadipic acid. A solution of 0.93 g (0.008 mole) of 1,6-hexanediamine and 1.0 g (0.018 mole) of potassium hydroxide in 80 ml of water was added at 0-10° with vigorous stirring to a solution of 2.6 g (0.008 mole) of perfluoroadipoyl chloride in 80 ml of carbon tetrachloride. The precipitate was filtered off, washed by decantation four times with methanol and then five times with water, and then dried in an Abderhalden pistol over P_2O_5 at 100°. We obtained 1.5 g (44.8%) of polyamide. Found: C 38.65; H 3.79; F 40.91%. $C_{12}H_{14}F_8N_2O_2$. Calculated: C 38.95; H 3.79; F 41.08%.

Polyamide from perfluorosebacic acid. In a similar way we prepared the polyamide formed by perfluorosebacic acid with 1,6-hexanediamine; yield 60.7%. Found: C 33.00; H 2.51; F 50.08%. $C_{16}H_{14}F_{16}N_2O_2$. Calculated: C 33.68; H 2.45; F 53.33%.

SUMMARY

1. By the telomerization of tetrafluoroethylene with 1,2-dichlorotrifluoroiodoethane a series of dichloropolyfluoroiodoalkanes $CF_2ClCFCl(CF_2CF_2)_nI$ ($\underline{n}$ = 1, 2, 3, and 4) were prepared.

2. Under the action of zinc the resulting dichloropolyfluoroiodoalkanes were converted into the corresponding tetrachloropolyfluoroalkanes and further into perfluoro α,ω-diolefins $CF_2 = CF(CF_2)_nCF = CF_2$ ($\underline{n}$ = 2, 3, 4, and 6).

3. Oxidation of the perfluoro α,ω-diolefins gave perfluoro dicarboxylic acids $HOOC(CF_2CF_2)_nCOOH$ ($\underline{n}$ = 2, 3, 4, and 6).

4. By the heterophase condensation of perfluoroadipoyl and of perfluorosebacoyl chloride with 1,6-hexanediamine, fluorinated polyamides were prepared.

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FLUORINE-CONTAINING β-SULTONES

COMMUNICATION 10. VALUE OF THE GROUP REFRACTION

OF FLUOROSULFONYL

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In previous communications we have described the reactions of fluorine-containing β-sultones with substances containing mobile hydrogen atoms (water, alcohols, thiols) [1-5]. By these reactions, and also by the further transformations of the products, we obtained some compounds that contained the fluorosulfonyl group. In the description of the physical properties of these compounds we gave, in particular, the values found for the specific gravity and refractive index. However, a comparison of the calculated and found values of the molecular refractions of these fluorosulfonyl compounds was not possible, because there was no information on the value of the refraction of this group in the available literature.

In the present paper we give a calculation of the value of the group refraction of fluorosulfonyl attached to carbon based on experimental values of specific gravity and refractive index for 16 liquid compounds derived from fluoro(fluorosulfonyl)acetic, difluoro(fluorosulfonyl)acetic, and tetrafluoro-2-(fluorosulfonyl)propionic acids, i.e., compounds of the general type $F-SO_2-X$, in which $X = CHF-CO-Y$, CF_2-CO-Y, or $CF(CF_3)-CO-Y$, Y being hydroxyl, anhydride O, Cl, alkoxyl, or alkylthio.

The value of the group refraction of fluorosulfonyl was determined as the difference between the molecular refraction found and the calculated value of the refraction of the group of atoms attached to sulfonyl and indicated here by X. The value of the refraction of this group of atoms was calculated from the values of atomic and group refractions given in Table 1 in accordance with data in the literature [6-9].

TABLE 1

Atom	R (cm^{-1})	Lit. ref.	Group of atoms	R (cm^{-1})	Lit. ref.
C	2,591	[6]	COO	6,200	[6]
H	1,028	[6]	CO	4,436	[6]
F	0,997	[7]	CH$_3$	5,653	[6]
F in RF	1,240	[8]	C$_2$H$_5$	10,300	[6]
Cl	4,436	[6]	n-C$_3$H$_7$	14,965	[6]
Cl in RCOCl	6,336	[9]	i-C$_3$H$_7$	14,975	[6]
S in RSH	7,729	[9]	n-C$_4$H$_9$	19,585	[6]

The values calculated in this way for the group refraction of fluorosulfonyl are given in Column 9 of Table 2. It will be seen that, with one exception (Compound 13), the values obtained for the refraction vary within the limits of double the experimental error (0.465 cm^{-1}; 4.4% of R) and may be averaged. The average value of the group refraction of fluorosulfonyl, calculated in accordance with the experimental data for 16 compounds (1-12, 14-17), is 10.541 cm^{-1}.

In Column 10 of Table 2 we give the calculated values of the molecular refractions, for which purpose the above-calculated value of the group refraction of fluorosulfonyl was used. It will be seen that the absolute departure of the values found for the molecular refractions from the calculated values (Column 11) does not exceed +0.181 cm^{-1} (Compound 12) and −0.347 cm^{-1} (Compound 1); here account must be taken of the fact that there are two fluorosulfonyl groups in the latter compound. The maximum relative departures (Column 12) are +0.79% (Compound 8) and −0.85% (Compound 1). Hence, the value that we have given for the group refraction of carbon-attached fluorosulfonyl is quite satisfactory for application in the physicochemical analysis of unknown compounds with the object of proving their structures, and also for the determination of the purity of substances of known structure. Thus, there can be no doubt that isopropyl difluoro(fluorosulfonyl)acetate (Compound 13), for which the difference between the found and calculated values of molecular refraction is almost 0.8 cm^{-1}, was isolated in an insufficiently pure state, and the physical constants given for this compound in the literature [4] are in need of correction.

TABLE 2

| No. | Compound | Mol. wt. | Exptl. values of | | Lit. ref. | MR found (cm^{-1}) | R_X (cm^{-1}) | R_{SO_2F} (cm^{-1}) | MR calc. (cm^{-1}) | Δ_{MR} | |
			n_D^{20}	d_4^{20}						(cm^{-1})	(%)
1	2	3	4	5	6	7	8	9	10	11	12
1	(FSO$_2$—CFH—CO)$_2$O	302,188	1,4102	1,8447	1	40,604	19,868*	10,368	40,951	−0,347	−0,85
2	FSO$_2$—CFH—CO—Cl	178,551	1,3845	1,6159	1	25,866	15,388	10,478	25,929	−0,063	−0,24
3	FSO$_2$—CFH—CO—OCH$_3$	174,128	1,3845	1,5060	1	27,162	16,469	10,693	27,010	+0,131	+0,48
4	FSO$_2$—CFH—CO—OC$_2$H$_5$	188,154	1,3880	1,3959	2	31,806	21,116	10,690	31,657	+0,149	+0,47
5	FSO$_2$—CFH—CO—SC$_3$H$_7$-n	218,238	1,4355	1,3456	3	42,364	31,746	10,618	42,287	+0,077	+0,18
6	FSO$_2$—CFH—CO—SC$_4$H$_9$-n	232,272	1,4355	1,2895	3	47,049	36,366	10,683	46,907	+0,142	+0,30
7	FSO$_2$—CFH—CO—SCH$_2$CH$_2$Cl	238,669	1,4600	1,5425	3	42,378	31,897	10,481	42,438	−0,060	−0,14
8	FSO$_2$—CFH—CO—OH	178,094	1,3602	1,7234	4	22,817	12,097	10,620	22,638	+0,179	+0,79
9	(FSO$_2$—CF$_2$—CO)$_2$O	338,172	1,3530	1,7441	4	42,035	20,778*	10,628	41,861	+0,174	+0,42
10	FSO$_2$—CF$_2$—CO—Cl	196,543	1,3570	1,6419	4	26,220	15,843	10,377	26,384	−0,164	−0,62
11	FSO$_2$—CF$_2$—CO—OCH$_3$	192,120	1,3510	1,5159	4	27,340	16,924	10,416	27,465	−0,125	−0,46
12	FSO$_2$—CF$_2$—CO—OC$_2$H$_5$	206,146	1,3565	1,3965	4	32,293	21,571	10,722	32,112	+0,181	+0,56
13	FSO$_2$—CF$_2$—CO—OC$_3$H$_7$-i	220,172	1,3595	1,3478	4	36,008	26,246	9,762**	36,787	−0,779	—
14	FSO$_2$—CF$_2$—CO—OC$_4$H$_9$-n	234,198	1,3719	1,2845	5	41,429	30,856	10,573	41,397	+0,032	+0,08
15	FSO$_2$—CF$_2$—CO—SC$_4$H$_9$-n	250,264	1,4100	1,3171	3	47,078	36,821	10,257	47,362	−0,284	−0,60
16	FSO$_2$—CF$_2$—CO—SCH$_2$CH$_2$Cl	256,661	1,4380	1,5763	3	42,744	32,352	10,392	42,893	−0,149	−0,35
17	FSO$_2$—CF(CF$_3$)—CO—OCH$_3$	242,130	1,3415	1,5600	2	32,664	21,995	10,669	32,536	+0,072	+0,22

* The values of R_X and R_{SO_2F} were calculated on the basis of the structure (FSO$_2$)$_2$X.

** This value of R_{SO_2F} was neglected in calculating the average value (R$_{SO_2F}$)m.

It must be pointed out also that the value cited for the group refraction of fluorosulfonyl is valid only for compounds containing this group linked with a carbon atom and is clearly not valid for other types of fluorosulfonyl compounds. This conclusion is supported by the following example of a departure from the additivity law. The difference between the group refractions of chlorosulfonyloxy in compounds of the chlorosulfonic ester type and of chlorosulfonyl attached to carbon in compounds of the alkanesulfonyl chloride type (16.37 and 15.40 cm^{-1} respectively; $\Delta = 0.97$ cm^{-1}) [10] differs from the value of the atomic refraction of ether oxygen (R = 1.764 cm^{-1}) [6]. An analogous departure from additivity is observed also in the case of dialkyl sulfates and alkyl alkanesulfonates (11.18 and 10.35 cm^{-1} respectively; $\Delta = 0.83$ cm^{-1}) [10]. In view of this it may be supposed that the value of the group refraction of fluorosulfonyloxy OSO_2F in compounds of the fluorosulfonic ester type will also exceed the value that we have given for the fluorosulfonyl group by an amount which is not equal to the atomic refraction of ether oxygen, but is 0.8 - 1.0 cm^{-1}, the total group refraction being about 11.4-11.5 cm^{-1}.

SUMMARY

A calculation was made of the group refraction of fluorosulfonyl attached to the carbon atom of an alkyl group; $R_{SO_2F} = 10.54$ cm^{-1}.

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THERMAL DECOMPOSITION OF ALKOXIDES DERIVED
FROM TERTIARY ALCOHOLS CONTAINING
TRIFLUOROMETHYL GROUPS

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It was recently found that, in the pyrolysis of salts of 3-hydroxy-3,3-bistrifluoromethylpropionic and 3-hydroxy-3-(trifluoromethyl)butyric acids, trifluoroacetone and acetone, respectively, were obtained in good yield [1]. It could be considered that the formation of ketones results from the simultaneous elimination of trifluoromethyl and carboxy groups, which is analogous to the removal of halogen and carbon dioxide in the decarboxylation of β-halo acids [2]

$$CF_3-\overset{\overset{\displaystyle R}{|}}{\underset{\underset{\displaystyle OH}{|}}{C}}-CH_2-\overset{\overset{\displaystyle O}{||}}{C}-\bar{O} \xrightarrow{200^\circ} \bar{C}F_3 + \overset{\overset{\displaystyle R}{|}}{\underset{\underset{\displaystyle OH}{|}}{C}}=CH_2 + CO_2 \qquad (1)$$

$$R=CF_3,\ CH_3$$
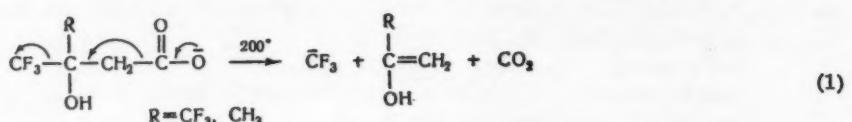
There is another possible mechanism, in which decarboxylation precedes the elimination of the trifluoromethyl group, and it would then be possible for alkoxides derived from tertiary alcohols to be formed as intermediate reaction products. The alkoxides could decompose further to ketones in a way analogous to that found in the case of alcohols containing trichloromethyl groups [3]

$$CF_3-\overset{\overset{\displaystyle R}{|}}{\underset{\underset{\displaystyle OH}{|}}{C}}-CH_2-CO\bar{O} \xrightarrow{-CO_2} \left[CF_3-\overset{\overset{\displaystyle R}{|}}{\underset{\underset{\displaystyle OH}{|}}{C}}-\bar{C}H_2 \to CF_3-\overset{\overset{\displaystyle R}{|}}{\underset{\underset{\displaystyle O}{|}}{C}}-CH_3 \right] \xrightarrow{\Delta} \bar{C}F_3 + RCOCH_3 \qquad (2)$$
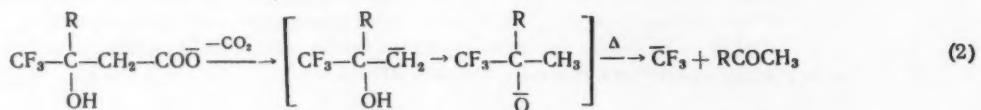
If it were found that the trifluoromethyl group is not eliminated from alkoxides derived from tertiary alcohols, then the third possible reaction mechanism, in which the elimination of the trifluoromethyl group precedes decarboxylation

$$CF_3-\overset{\overset{\displaystyle R}{|}}{\underset{\underset{\displaystyle OH}{|}}{C}}-CH_2-CO\bar{O} \to \left[\begin{matrix} \bar{C}F_3 + RCOCH_2COOH \\ \downarrow \\ RCOCH_3 + CO_2 \end{matrix} \right] \qquad (3)$$
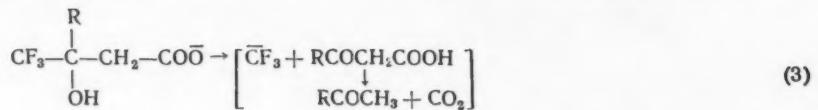
need not be considered since it would be expected that the mobility of the CF_3 group would be less in hydroxy acids than in alkoxides

$$\overset{\frown}{CF_3}-\overset{\overset{\displaystyle R}{|}}{\underset{\underset{\displaystyle OH}{|}}{C}}-CH_2CO\bar{O} \qquad \text{и} \qquad \overset{\frown}{CF_3}-\overset{\overset{\displaystyle R}{|}}{\underset{\underset{\displaystyle O}{|}}{C}}-CH_3$$
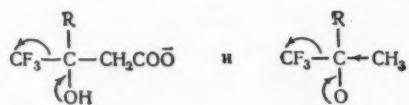
In order to make a choice between the possible reaction mechanism (1), (2), and (3), we synthesized alkoxides derived from methylbistrifluoromethylmethanol (I) and dimethyl(trifluoromethyl)methanol (II)

$$
\begin{array}{cc}
CH_3 & CH_3 \\
| & | \\
CF_3-C-OK & CF_3-C-OK \\
| & | \\
CF_3 & CH_3 \\
(I) & (II)
\end{array}
$$
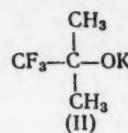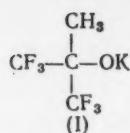
and investigated their thermal decomposition under the conditions used for the decomposition of salts of β-hydroxy acids.

It was found that in the alkoxide (II) the trifluoromethyl group has pseudohalogen properties, and in this case we isolated acetone from the reaction mixture in 49% yield

$$
CF_3-C-\bar{O} \longrightarrow \bar{C}F_3 + CH_3COCH_3
$$
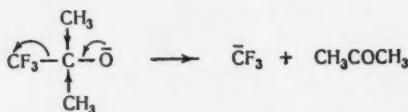
In the case of the methylbistrifluoromethylmethoxide, however, not even traces of the expected trifluoroacetone were obtained; the conjugation of the trifluoromethyl group with only three hydrogen atoms in this alkoxide is clearly insufficient to make it mobile

$$
CF_3-C-\bar{O} \quad\xrightarrow{\quad\times\quad} \quad \bar{C}F_3 + CF_3COCH_3
$$
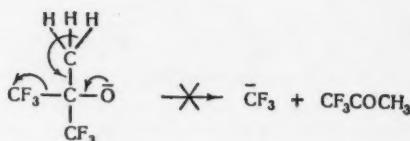
The alkoxide (I) cannot therefore be an intermediate product of the pyrolysis of 3-hydroxy-3,3-bistrifluoromethylpropionic acid. This view is supported also by the fact that on pyrolysis both alkoxides are converted in part into the corresponding tertiary alcohols, whose formation is not observed in the decomposition of the salts of hydroxy acids

$$
\begin{array}{ccc}
R & & R \\
| & 200° & | \\
CF_3-C-OK & \longrightarrow & CF_3-C-OH \\
| & & | \\
CH & & CH_3
\end{array}
\quad \text{in which } R = CH_3 \text{ and } CH_3
$$
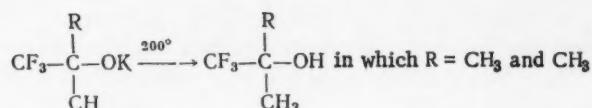
Such an unusal reaction immediately prompts the suspicion that the alkoxides contain water, but repetition of the experiments with reactants prepared in a way that excluded the introduction of moisture* did not lead to any change in result.

Another example of an analogous reaction is known. In the pyrolysis of sodium trifluoroethoxide and sodium heptafluorobutoxide the corresponding fluoro alcohols were obtained [4]

$$
CF_3CH_2ONa \rightarrow CF_3CH_2OH \text{ и } NaF
$$
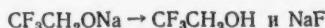
the formation of which is explained by the authors on the view that the alkoxide ion abstracts a proton from the α-position of a neighboring molecule with formation of the alcohol and another anion which has its negative charge on a carbon atom and is so able to become stabilized by the elimination of a fluoride ion

---

* The alkoxides were prepared by the reaction of potassium with the absolutely dry alcohol, which was taken in excess, with subsequent purification, either by vacuum drying, or by recrystallization from dry benzene.

$$CF_3CH_2\overline{O} + CF_3CH_2ONa \rightarrow CF_3CH_2OH + CF_3\overline{C}HONa$$
$$CF_3\overline{C}HONa \rightarrow CF_2{=}CH{-}ONa + \overline{F}$$
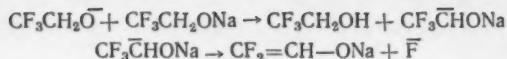
In the alkoxides derived from tertiary fluoro alcohols investigated by us there is no hydrogen atom in the α-position to oxygen, so that this reaction mechanism is not applicable in the present case.

Hence, analysis of the products of the pyrolysis of the alkoxides derived from methylbistrifluoromethyl- and dimethyl(trifluoromethyl)methanols enables us to make our choice in favor of mechanism (1) for the thermal decomposition of salts of 3-hydroxy-3,3-bistrifluoromethylpropionic and 3-hydroxy-3-(trifluoromethyl)butyric acids, in which the formation of ketones results from the simultaneous elimination of carbon dioxide and the trifluoromethyl group.
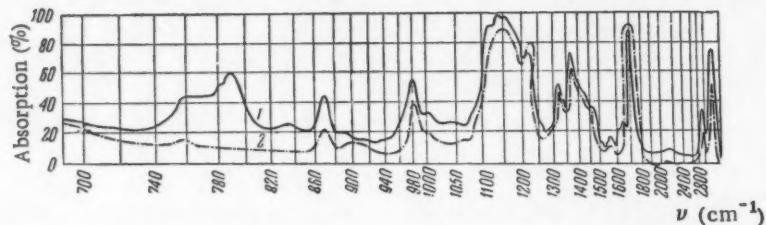
Infrared spectra: 1) Fraction of b.p. 55-90°; 2) mixture of acetone and dimethyl(trifluoromethyl)methanol.

EXPERIMENTAL

Methylbistrifluoromethylmethanol. This was synthesized by a previously described method [5], but was inadequately pure and contained traces of iodine: for purification it was shaken with mercury until decolorized, filtered, and distilled through a rectification column from its mixture with concentrated sulfuric acid. However, even after a repeat of the purification operation we did not succeed in freeing the alcohol from impurities; thus the alcohol obtained after the pyrolysis was found to be purer and differed somewhat in refractive index from that taken for the preparation of the alkoxide and from that described in the literature. The original material had the following constants: b.p. 61-62°; n_D^{20} 1.3004. The literature [5] gives: b.p. 60.5-61.5°; n_D^{20} 1.3030; d_4^{20} 1.4840.

Potassium methylbistrifluoromethylmethoxide. A round-bottomed flask fitted with reflux condenser was charged with 40 ml of dry benzene, 38 g (0.21 mole) of methylbistrifluoromethylmethanol, and 7.5 g (0.19 g-atom) of potassium. When the potassium had dissolved completely, the precipitate of alkoxide was filtered off and dried in a vacuum (1 mm) at 100° for three hours. We obtained 40 g of the alkoxide (I) as an infusible slightly hygroscopic white powder.

Pyrolysis of potassium methylbistrifluoromethylmethoxide. The pyrolysis was carried out in a Pyrex flask connected to three traps, the first of which was at room temperature and the other two were cooled with a mixture of solid carbon dioxide and acetone. The flask was heated carefully in a metal bath: the decomposition of the alkoxide set in suddenly at 220° and proceeded very vigorously. From 36.5 g (0.17 mole) of the alkoxide we obtained 20.6 g of brown liquid, which was fractionated through a standard 400 mm column; we then isolated 10 g of methylbistrifluoromethylmethanol; b.p. 61-62°; n_D^{20} 1.2970. Found: C 26.26; H 2.17; F 62.06%. $C_4F_6H_4O$. Calculated: C 26.14; H 2.19; F 62.40%. Most of the residue was alkoxide that had sublimed during the pyrolysis.

Dimethyl(trifluoromethyl)methanol. This was purified by distillation from concentrated sulfuric acid with subsequent crystallization from octane and distillation through a column. It had the following constants: b.p. 82.0°; n_D^{20} 1.3365; m.p. 19-21°. The literature [6] gives: b.p. 81.6-81.7° (761 mm); $n_D^{22.6}$ 1.3324; m.p. 20.75°.

Potassium dimethyl(trifluoromethyl)methoxide. In 38.2 g (0.3 mole) of dimethyl(trifluoromethyl)methanol we dissolved 6.3 g (0.16 g-atom) of potassium, after which the excess of the alcohol was vacuum-distilled off and the alkoxide was dried at 100° and 0.1 mm for eight hours. We obtained 27.38 g of the alkoxide (the amount calculated from the amount of potassium taken was 26.85 g). In another experiment the alkoxide was purified by crystallization from dry benzene.

Pyrolysis of potassium dimethyl(trifluoromethyl)methoxide. The pyrolysis of 27.4 g of the alkoxide (II) in a dry nitrogen atmosphere was carried out in the same apparatus as that of the alkoxide (I). We obtained 18.0 g of liquid and 7.3 g of dry residue. The liquid was fractionated through a standard column, and the following fractions were collected: Fraction I (2 g), b.p. 54° (756 mm), was acetone and was characterized by conversion into its 2,4-dinitrophenylhydrazone; Fraction II (2 g), b.p. 54-80°, was an intermediate fraction; Fraction III (11 g), b.p. 80-82°, was a mixture of acetone and dimethyl(trifluoromethyl)methanol, which was shown to contain 1.7 g of acetone from the results of the treatment of a sample of this mixture with excess of 2,4-dinitrophenylhydrazine. After crystallization of Fraction III from octane we obtained the pure alcohol, which showed no depression of melting point in admixture with a known sample.

In an analogous way it was found that Fraction II contained acetone and the alcohol in the ratio of 1 : 1. Hence, the total amount of acetone was 4.7 g (49%) and the amount of dimethyl(trifluoromethyl)methanol 10.2 g. Analogous results were obtained also in the pyrolysis of the alkoxide that was first crystallized from benzene.

In another experiment the liquid obtained after the pyrolysis was distilled; one fraction of b.p. 55-90° was collected, and the infrared spectrum of this closely resembled the spectrum of a mixture prepared from acetone and dimethyl(trifluoromethyl)methanol in the ratio of 1 : 2.

SUMMARY

1. An investigation was made of the thermal decomposition of methylbistrifluoromethyl- and dimethyl(trifluoromethyl)-methoxides, which led to the formation of the corresponding tertiary alcohols.

2. In the dimethyl(trifluoromethyl)methoxide the trifluoromethyl group has pseudohalogen properties.

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STEREOCHEMISTRY OF CYCLIC COMPOUNDS

COMMUNICATION 41. SYNTHESIS OF GEOMETRIC ISOMERS OF HEXAHYDRO- AND OCTAHYDRO-7-METHOXY-1,2-PHENANTHRENEDICARBOXYLIC ACIDS

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As shown previously [1], the main product of the diene condensation of 3,4-dihydro-6-methoxy-1-vinyl-naphthalene (I) with maleic anhydride is the cis-syn anhydride (II) (up to 65%), m.p. 204°, whose configuration corresponds to its formation by the normal scheme of endo-cis addition. We did not succeed in detecting the other possible isomer (cis-anti), and the extent to which this reaction proceeds contrary to the "accumulation of unsaturation" rule was left open. The necessity of synthesizing large amounts of the cis-syn anhydride (II) made it possible for us to accumulate mother liquors obtained in the crystallization of the crude cis-syn adduct from dioxane, which enabled us to make a more detailed study of the composition of the products of this interesting diene reaction. From the combined mother liquors remaining after the separation of about 225 g of pure cis-syn adduct (II) we obtained 3.2 g of an individual crystalline compound, m.p. 189.5-191°, which corresponded in analysis to the adduct, but differed from all previously synthesized anhydrides [1] and had two absorption maxima in the ultraviolet (266.5 and 295.0 mμ) characteristic for derivatives of hexahydro-7-methoxy-1,2-phenanthrenedicarboxylic acid containing a 4,4a double bond [1, 2]. The structure and configuration of this compound as the cis-anti anhydride (III) was proved unequivocally by the displacement of its double bond with formation of the cis anhydride (IV), which had been prepared previously by this reaction from the cis-syn anhydride (II) [1, 2]
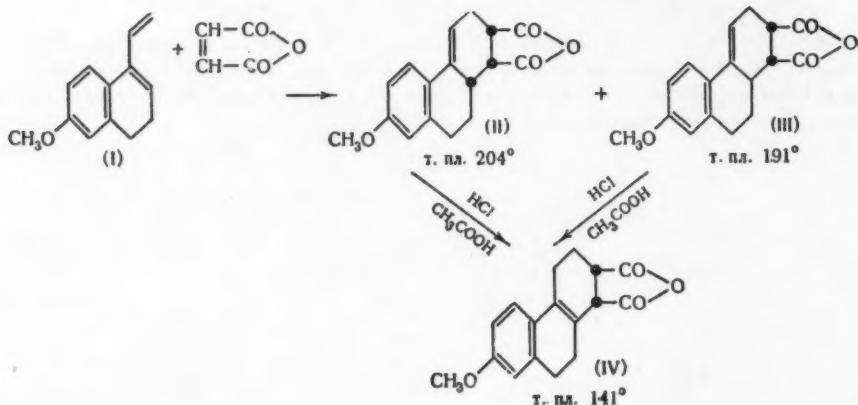
This fact shows that the anhydrides (II) and (III) are epimers with respect to C—10a, so that the isomer (III) has the only possible cis-anti configuration. Hence, we have established that the diene condensation of 3,4-dihydro-6-methoxy-1-vinylnaphthalene with maleic anhydride, though proceeding sterically selectively and giving mainly the cis-syn adduct (II), even under mild conditions is accompanied by the formation of the cis-anti adduct, the ratio of the amounts of these isomers being about 70 : 1.

Hydrolysis of the cis-anti anhydride (III) by boiling it with aqueous dioxane leads to the smooth formation of the corresponding cis-anti acid (V), which gives the crystalline dimethyl ester (VI) on treatment with diazomethane
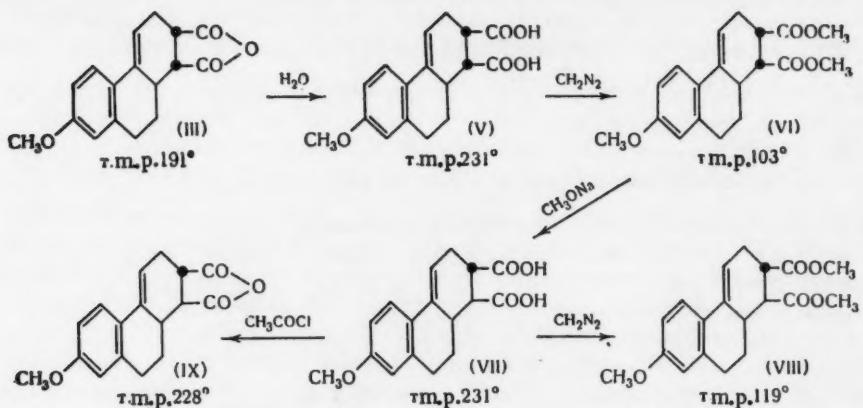
Isomerization of the cis-anti diester (VI) with sodium methoxide gave a good yield of the new acid (VII), which differed from all the acids described previously [1] and gave crystalline diester (VIII) and anhydride (IX). In accordance with the method of its preparation this acid should have a trans-syn configuration. In this way we completed the synthesis of all four theoretically possible geometric isomers of 1,2,3,9,10,10a-hexahydro-7-methoxy-1,2-phenanthrenedicarboxylic acid [1].

As the cis-anti acid (V) is extremely poorly soluble in the usual organic solvents, for the preparation of new geometric isomers of 1,2,3,4,4a,9,10,10a-octahydro-7-methoxy-1,2-phenanthrenedicarboxylic acid it was hydro-

genated in the form of the water-soluble disodium salt. It was found that in this case the hydrogenation proceeds sterically nonselectively, and the smooth addition of one molecular proportion of hydrogen gives a crystalline mixture of both possible isomers: the cis-anti-trans acid (X) and the previously described [3] cis-anti-cis acid (XI)
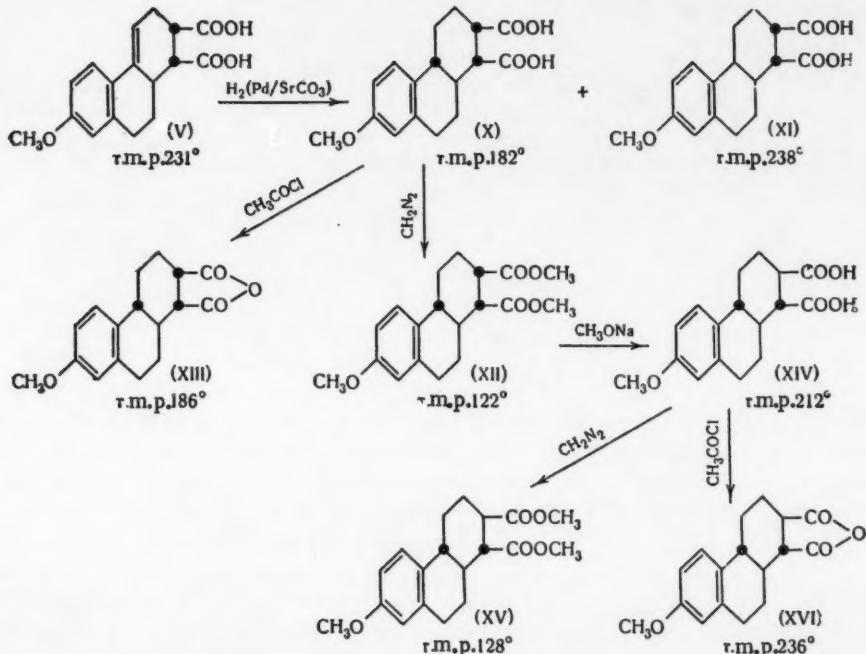
1375

in a ratio of about 12 : 1. The quantitative separation of these acids was readily carried out as a result of the extremely low solubility of the cis-anti-cis acid (XI) in acetone. The sterically nonselective hydrogenation of compounds of exo configuration has been previously noted by us [4] for the case of cis-trans-3,4-dimethyl-4-cyclohexene-1,2-dicarboxylic acid, in which the corresponding saturated isomers were formed in the ratio of 1 : 2. However, the hydrogenation of both the isomers of 1,2,3,5,6,7,8,8a-octahydro-1,2-naphthalenedicarboxylic acid proceeds selectively [5]. The new cis-anti-trans acid (X) was characterized as its dimethyl ester (XII) and anhydride (XIII).

Isomerization of the cis-anti-trans diester (XII) with sodium methoxide readily gives a high yield of the new acid (XIV), which has trans union of the rings and should possess the more thermodynamically favored trans-anti-trans configuration. On treatment with diazomethane this acid gives the trans-anti-trans diester (XV), and on being boiled with acetyl chloride it forms the trans-anti-trans anhydride (XVI).

Finally, it was of interest to study the possibility of ionic trans reduction of the double bond in the cis anhydride (IV), which could give two different geometric isomers with trans union of the rings. The performance of this reaction presented some difficulty since, under the conditions of Birch's reaction (use of excess of lithium in liquid ammonia), partial reduction of the aromatic ring might occur and, moreover, the carboxy groups should be attacked. We succeeded in carrying out this reaction in a relatively selective manner only by the use of three moles of lithium per mole of the cis anhydride (IV). From the mixture of reduction products then formed (after hydrolysis and treatment with diazomethane) we succeeded in isolating a mixture of approximately equal amounts of the above-described cis-anti-trans diester (XII) and a new diester (XVII), m.p. 89°, in a total yield of up to 30%.

On isomerization with sodium methoxide and treatment with diazomethane this last compound gave the trans-anti-trans diester (XV), which was obtained above in the analogous isomerization of the cis-anti-trans diester (XII). This fact gave reason to suppose that the new diester (XVII) has the cis-syn-trans configuration, as only then may be explain its formation in the complete reduction of the cis anhydride (IV) and its conversion into the trans-anti-trans isomer.

Hence, for the case of the reduction of the anhydride (IV) with lithium in liquid ammonia we have established the interesting fact of the simultaneous formation of both possible isomers with trans union of rings B and C.
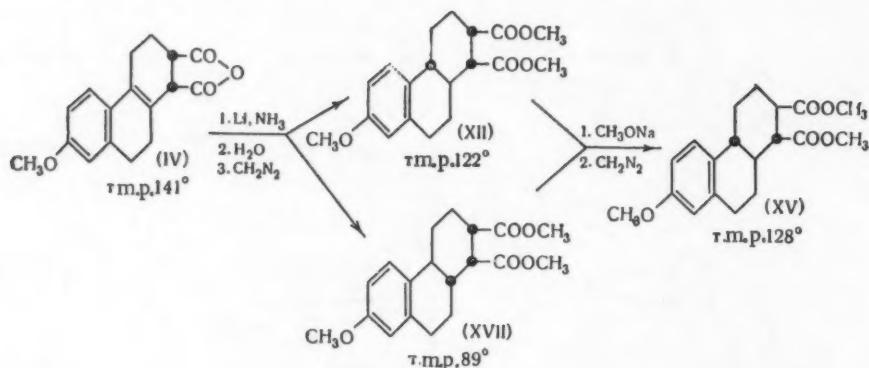
As already stated [1], in the catalytic hydrogenation of such compounds the cis addition of hydrogen occurs only from the side opposed to the carboxy groups. As the result of our investigations (see also [3]), we have synthesized seven of the eight possible geometric isomers of 1,2,3,4,4a,9,10,10a-octahydro-7-methoxy-1,2-phenanthrenedicarboxylic acid, the configurations of which have been confirmed by their mutual transformations.

EXPERIMENTAL*

cis-anti Anhydride (III). The mother liquors remaining from the crystallization from dioxane of the cis-syn anhydride (II) obtained in ten analogous experiments [1] from about 240 g of 3,4-dihydro-6-methoxy-1(2H)-haphthalenone were combined and evaporated down to low bulk. When the solution was allowed to stand for several days, there separated a bright-yellow crystalline substance, m.p. 172-180°, from which by crystallization from

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* All melting points are corrected.

acetone we obtained 3.2 g of the cis-anti anhydride (III), m.p. 186-188°. Recrystallization from acetone gave an analytically pure sample of the cis-anti anhydride (III) as bright-yellow needles, m.p. 189.5-191°, depressed by admixture of the isomeric cis-syn anhydride (II) (165-175°). Ultraviolet spectrum (in acetonitrile): λ^1_{max} 266.5 mμ (log ε 4.268); λ^2_{max} 295.0 mμ (log ε 3.666). Found: C 71.87, 72.00; H 5.66, 5.60%. $C_{17}H_{16}O_4$. Calculated: C 71.80; H 5.67%.

cis Anhydride (IV). A mixture of 0.2 g of the cis-anti anhydride (III) and 3.0 ml of a saturated solution of dry hydrogen chloride in a mixture of 2 parts of acetic anhydride and 1 part of acetic acid was heated for one hour at 60°. Solvents were vacuum-distilled off, and the crystalline residue was washed on the filter with a 1 : 1 mixture of acetone and ether; we obtained 0.16 g of the cis anhydride (IV), m.p. 133-136°. After two crystallizations from 1 : 1 acetone-ether it melted at 139-140° and showed no depression of melting point in admixture with a known sample of the cis anhydride (IV) [1]. Ultraviolet spectrum (in acetonitrile): λ_{max} 281.5 mμ (log ε 4.233).

cis-anti Acid (V). A mixture of 2.65 g of the cis-anti anhydride (III), 1.5 ml of water, and 15 ml of dioxane was boiled for four hours, and the crystals that separated were filtered off; we obtained 1.65 g of the cis-anti acid (V), m.p. 222-225° (decomp.). The filtrate was vacuum-evaporated to dryness, and the crystalline residue was washed on the filter with 50% dioxane; we obtained a further 1.02 g of colored cis-anti acid (V), m.p. 214-217°, which after crystallization from 85% dioxane melted at 226-228° (0.85 g). Recrystallization from dioxane gave the pure cis-anti acid, m.p. 230-231° (decomp.). Found: C 67.50, 67.38; H 6.09, 6.06%. $C_{17}H_{18}O_5$. Calculated: C 67.53; H 6.00%.

cis-anti Diester (VI). A suspension of 0.85 g of the cis-anti acid (V) in methanol was treated with ethereal diazomethane. We obtained 0.88 g of the cis-anti diester (VI), m.p. 99-101°. On crystallization from methanol the cis-anti diester (VI) formed fine needles, m.p. 102-103°. Found: C 69.10, 68.96; H 6.74, 6.66%. $C_{19}H_{22}O_5$. C lculated: C 69.07; H 6.71%.

trans-syn Acid (VII). To a solution of sodium methoxide (from 1.44 g of sodium) in 30 ml of absolute methanol we added 0.60 g of the cis-anti diester (VI), and the mixture was boiled for 12 hours. Methanol was vacuum-distilled off, the residue was dissolved in 150 ml of water, and the solution was filtered and evaporated in a porcelain dish on a water bath. The precipitate of salts was washed on the filter with methanol and dissolved in 45 ml of water; the solution was filtered and acidified with hydrochloric acid. The finely crystalline precipitate was filtered off, washed with water, and dried in air. We obtained 0.47 g of the trans-syn acid, m.p. 230-232° (decomp.), which after crystallization from dioxane melted at 232.5-233° (decomp.). Found: C 67.08, 67.04; H 6.02, 6.02%. $C_{17}H_{18}O_5$. Calculated: C 67.53; H 6.00%.

trans-syn Diester (VIII). A suspension of 0.15 g of the trans-syn acid (VII) in methanol was treated with ethereal diazomethane; we obtained 0.12 g of the trans-syn diester (VIII), m.p. 118-120°, which crystallized from methanol in the form of scales melting constantly at 118-119°. Found: C 69.07, 69.18; H 6.86, 6.72%. $C_{19}H_{22}O_5$. Calculated: C 69.07; H 6.71%.

trans-syn Anhydride (IX). A mixture of 0.20 g of the trans-syn acid (VII) and 8 ml of acetyl chloride was boiled until solution was complete (three hours), and acetyl chloride was then vacuum-distilled off; after repeated evaporation with benzene the residue crystallized out. It was washed on the filter with ether, and we obtained 0.13 g of the trans-syn anhydride (IX); small yellow needles (from benzene), m.p. 227-228°. Found: C 71.64, 71.58; H 5.68, 5.68%. $C_{17}H_{16}O_4$. Calculated: C 71.80; H 5.67%.

cis-anti-trans Acid (X). To a solution of 0.45 g of sodium hydroxide in 15 ml of water we added 1.5 g of the cis-anti acid (V); the mixture was heated carefully until solution occurred, and was then filtered. To the solution of the disodium salt of the anti-cis acid (V) so obtained we added 0.4 g of 30% Pd/SrCO$_3$ [6], and the salt was hydrogenated at room temperature, when 145 ml (22°, 743 mm) of hydrogen was absorbed. The catalyst was filtered off, the filtrate was added slowly to 20 ml of 3% hydrochloric acid, and the crystals were filtered off, washed with water, and dried in air. The hydrogenation product (1.45 g, m.p. 180-200°) was extracted with 20 ml of boiling acetone, and the undissolved part was filtered off. We obtained 0.11 g of the previously described [3] cis-anti-cis acid (XI), decomp. temp. 237-238°, which showed no depression of melting point in admixture with a known sample. The acetone filtrate was evaporated down to about 7 ml and diluted with 5 ml of water; we obtained 1.12 g of the cis-anti-trans acid (X), m.p. 182-183° (decomp.). On evaporation of the mother liquor we isolated a further 0.15 g of the acid (X), m.p. 180-182°. After crystallization from 60% acetone the pure cis-anti-trans acid (X) was obtained as fine gleaming crystals, m.p. 181.5-182.5° (decomp.). Found: C 66.89, 66.75; H 6.65, 6.57%. $C_{17}H_{20}O_5$. Calculated: C 67.09; H 6.62%.

cis-anti-trans Diester (XII). A solution of 0.90 g of the cis-anti-trans acid (X) in methanol was treated with ethereal diazomethane. We obtained 0.85 g of the cis-anti-trans diester (XII), m.p. 121-122°, which after crystallization from methanol formed very fine long needles with the same melting point. Found: C 68.95, 68.97; H 7.38, 7.62%. $C_{19}H_{24}O_5$. Calculated: C 68.65; H 7.28%.

cis-anti-trans Anhydride (XIII). A mixture of 0.18 g of the cis-anti-trans acid (X) and 3 ml of acetyl chloride was boiled for one hour; we obtained 0.15 g of the cis-anti-trans anhydride (XIII), m.p. 178-180°. Crystallization from a 1 : 1 mixture of benzene and petroleum ether gave the pure cis-anti-trans anhydride (XIII), m.p. 185-186° (fine needles). Found: C 71.43, 71.56; H 6.45, 6.51%. $C_{17}H_{18}O_4$. Calculated: C 71.31; H 6.34%.

trans-anti-trans Acid (XIV). To a solution of sodium methoxide (from 1.7 g of sodium) in 35 ml of absolute methanol we added 0.70 g of the cis-anti-trans diester (XII), and the mixture was boiled for 23 hours. Methanol was vacuum-distilled off, the residue was dissolved in water (70 ml), and the solution was filtered and evaporated in a porcelain dish on a water bath. The precipitate of salts was dissolved in water (15 ml), and the solution was filtered and carefully added to excess of dilute hydrochloric acid. When the solution stood for one day the trans-anti-trans acid (XIV) separated in the form of flocs, which were filtered off, washed with water, and dried. We obtained 0.53 g of reaction product, m.p. 194-200°, which was dissolved in 4 ml of 50% acetone, and the solution evaporated down slightly. On standing 0.14 g of the monoester of the trans-anti-trans acid, m.p. 176-179°, crystallized out in the form of fine needles, which after recrystallization from 50% acetone melted without decomposition at 184-185°. The structure of this monoester was not studied. Found: C 67.47, 67.49; H 6.93, 6.97%; M 312.4. $C_{18}H_{22}O_5$. Calculated: C 67.90; H 6.97%; M 318.4. On careful evaporation of the mother liquor and subsequent long standing there separated 0.30 g of the trans-anti-trans acid (XIV) in the form of fine compact crystals, m.p. 208-211°, which after crystallization from 50% acetone melted at 210-212°. Found: C 66.97, 66.88; H 6.69, 6.72%. $C_{17}H_{20}O_5$. Calculated: C 67.09; H 6.62%.

trans-anti-trans Diester (XV). A suspension of 0.10 g of the monoester of the trans-anti-trans acid in methanol was treated with ethereal diazomethane. We obtained 0.09 g of the trans-anti-trans diester (XV), which on crystallization from methanol formed transparent plates, m.p. 127-128°. Found: C 68.74, 68.81; H 7.29, 7.24%. $C_{19}H_{24}O_5$. Calculated: C 68.65; H 7.28%.

A suspension of 0.06 g of the trans-anti-trans acid (XIV) in methanol was treated with diazomethane in an analogous manner; we obtained 0.06 g of the trans-anti-trans diester (XV), m.p. 127-128°, undepressed by admixture of the sample described above.

trans-anti-trans Anhydride (XVI). A mixture of 0.14 g of the trans-anti-trans acid (XIV) and 3.0 ml of acetyl chloride was boiled for one hour; we obtained 0.09 g of the trans-anti-trans anhydride (XVI), m.p. 230-232°, which after crystallization from dioxane formed compact glistening crystals, m.p. 234-236°. Found: C 71.18, 71.04; H 6.58, 6.47%. $C_{17}H_{18}O_4$. Calculated: C 71.31; H 6.34%.

Reduction of the cis anhydride (IV) with lithium in liquid ammonia. A solution of 3 g of the cis anhydride (IV) in 70 ml of dry tetrahydrofuran was added slowly with stirring to 100 ml of liquid ammonia cooled to −50°, and then 150 mg of lithium cut into fine pieces was added. The reaction mixture was stirred for 15 minutes and then decomposed by the addition of 3 g of ammonium chloride; liquid ammonia and tetrahydrofuran were removed by the passage of ammonia. The dry residue was treated with 50 ml of 0.5% hydrochloric acid, and the precipitate was filtered off and dissolved in 50 ml of methanol; the solution was boiled with 30 ml of 3 N HCl for three hours, and solvents were vacuum-distilled off. The residue was treated with ether, and the undissolved part was filtered off (0.5 g, m.p. 175-220°) and boiled with acetone; we obtained 0.30 g of a nitrogen-containing compound (Lassaigne's test), m.p. 244-245°, which was not investigated further. On dilution of the acetone filtrate with water there separated 0.15 g of crystalline substance (m.p. 184-185° after crystallization from 60% acetone), the treatment of which with ethereal diazomethane gave the cis-syn-trans diester (XVII), m.p. 86-88°. Crystallization from methanol gave an analytically pure sample of the diester (XVII), m.p. 88-89°. Found: C 68.61, 68.42; H 7.02, 7.10%. $C_{19}H_{24}O_5$. Calculated: C 68.65; H 7.28%.

The ethereal mother solution(see above) was treated with diazomethane solution, solvent was evaporated off, and the oily residue was dissolved in the minimum amount of methanol. After one day the solution yielded a precipitate of 0.35 g of the above-described cis-anti-trans diester (XII), m.p. 121-122°, undepressed by admixture of a known sample. On keeping the mother liquor at 0° for one day we obtained a further 0.15 g of the cis-anti-trans diester (XII), m.p. 118-119°. On keeping the solution at 0° for another week we separated 0.60 g of a crystalline

substance, m.p. 65-70°, the crystallization of which from methanol gave 0.35 g of the above-described cis-syn-trans diester (XVII), m.p. 87.5-89°, undepressed by admixture with a known sample. All the mother solutions were combined and evaporated to dryness; the residue was added to a solution of sodium methoxide (from 5.1 g of sodium) in 60 ml of absolute methanol, and the mixture was boiled for 26 hours. Methanol was vacuum-distilled off, the residue was dissolved in 15 ml of water, and the solution was acidified with dilute hydrochloric acid and vacuum-evaporated to dryness. The residue was extracted with acetone and treated with ethereal diazomethane; solvents were distilled off, and the oily residue was treated with methanol. We obtained 0.1 g of the above-described trans-anti-trans diester (XV), m.p. 126-127°, undepressed by admixture of a known sample.

Isomerization of the cis-syn-trans diester (XVII). A mixture of 0.20 g of the cis-syn-trans diester (XVII) and a solution of sodium methoxide (from 0.4 g of sodium) in 15 ml of absolute methanol was boiled for 26 hours and treated as described in the previous experiment. We isolated 0.15 g of the trans-anti-trans diester (XV), m.p. 127-128°, undepressed by admixture of the sample obtained by the analogous isomerization of the cis-anti-trans diester (XII).

SUMMARY

1. The diene condensation of 3,4-dihydro-6-methoxy-1-vinylnaphthalene with maleic anhydride proceeds with the formation of both possible stereoisomers of the product: the cis-syn anhydride (II) and the cis-anti anhydride (III) in the ratio 70 : 1.

2. By series of transformations the syntheses were carried out of cis-anti- and trans-syn-1,2,3,9,10,10a-hexahydro-7-methoxy-1,2-phenanthenedicarboxylic acids (V) and (VII) and of cis-anti-trans-, cis-syn-trans- (as the diester), and trans-anti-trans-1,2,3,4,4a-9,10,10a-octahydro-7-methoxy-1,2-phenanthrenedicarboxylic acids (X), (XVII) (diester), and (XIV).

3. Unlike catalytic hydrogenation reduction of the 4a, 10a double bond (interring) in cis-1,2,3,4,9,10-hexahydro-7-methoxy-1,2-phenanthrenedicarboxylic anhydride under ionic conditions leads to a mixture of both possible isomers in the trans configuration.

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β-DICARBONYL COMPOUNDS*

COMMUNICATION 9. REACTION OF β-DICARBONYL COMPOUNDS
WITH HYDROGEN PEROXIDE

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In a previous investigation we studied the reactions of some β-dicarbonyl compounds with hydrogen peroxide in an alkaline medium [1]. It was shown that under these conditions 1,3-cyclohexanedione forms glutaric acid, but dimedon (5,5-dimethyl-1,3-cyclohexanedione) gives a mixture of 2-hydroxybidimedon [1-hydroxy-4,4,4',4'-tetra-methyl-2,2',6,6'-(bicyclohexyl)tetrone] (I) and 3,3-dimethylglutaric acid in the ratio 4.5 : 1
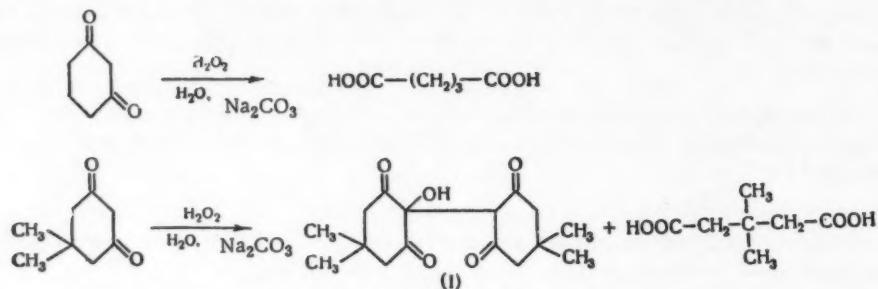
It was shown also that the 2-oxo derivatives of cyclohexane- and cyclopentane-carboxaldehydes behave in a peculiar fashion toward alkaline hydrogen peroxide and are converted by oxidative cleavage into pimelic and adipic acids.

In the present work we have continued the study of the oxidation of β-dicarbonyl compounds with hydrogen peroxide and examined the effect of alkali on the course of this reaction. In absence of alkali the oxidation of 1,3-cyclohexanedione and dimedon proceeds very slowly and leads to glutaric and 3,3-dimethylglutaric acids in yields of about 50%. In the case of 2-oxocycloalkanecarboxaldehydes the addition of alkali does not have any appreciable effect on the course of the reaction. 2-Oxocyclopentanecarboxaldehyde passes almost quantitatively into adipic acid; 2-oxocyclohexanecarboxaldehyde and its methyl derivatives form mixtures of pimelic and cyclopentanecar-boxylic acids in proportions that depend on the presence of CH₃ groups in the original substance. Higher yields of dicarboxylic acids are given by 4- and 5-methyl-2-oxocyclohexanecarboxaldehydes. Judging by the melting points of the corresponding amides, both of the methylcyclopentanecarboxylic acids that we obtained belong to the trans series.

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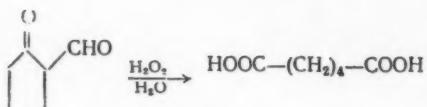
* Continuation of series of papers on the chemistry of 1,3-cyclohexanedione. For Communication 8 see Zhurnal Obshchei Khimii 30, 3658 (1960).
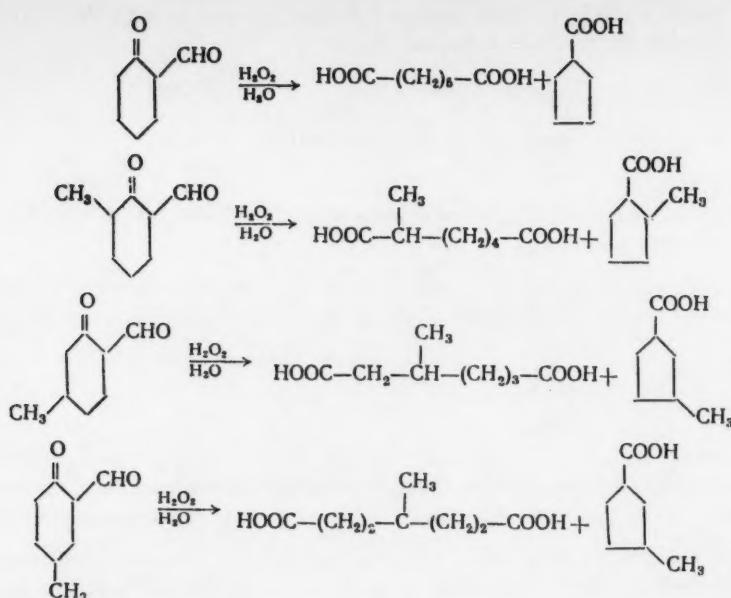
This transformation of 2-oxocyclohexanecarboxaldehydes into cyclopentanecarboxylic acids is reminiscent of Favorskii's reaction and the oxidative rearrangement of ketones accompanied by ring contraction. Thus, under the action of sodium methoxide 2-chlorocyclohexanone and its methyl derivatives pass into the corresponding cyclopentane-carboxylic acids [2-4].

Cyclopentanecarboxylic acid is formed also in the reaction of cyclohexanone with hydrogen peroxide in pyridine [5, 6]. A case of ring contraction is found also in the treatment of the β-diketone (II) with hydrogen peroxide in acetic acid [7]:
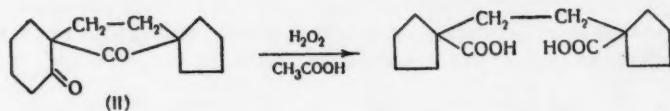
The reaction of oxocyclohexanecarboxaldehydes with hydrogen peroxide may serve as a convenient method for the preparation of pimelic acids. In its simplicity and in the availability of the reactants, this method is not inferior to those described in the literature [8], which are based on the cleavage of ethyl 2-oxocyclohexanecarboxylate and salicylic acid:
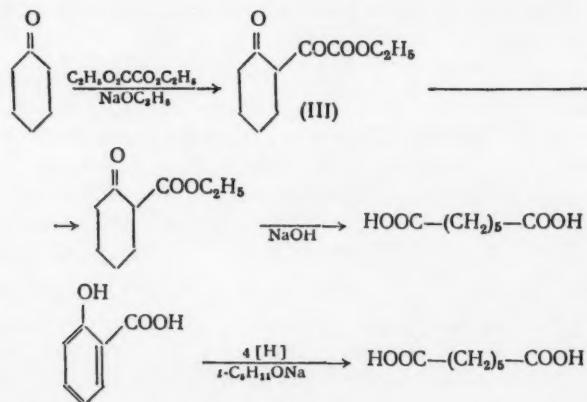
On the oxidation of benzoylacetaldehyde with alkaline hydrogen peroxide, in addition to an oily product that has not been investigated further, benzoic acid is formed:
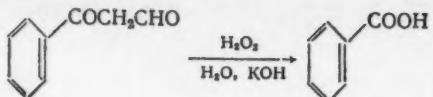
Under the action of hydrogen peroxide in presence or absence of alkali 2-acetyl-1,3-cyclohexanedione (IV) undergoes oxidative cleavage to glutaric acid:
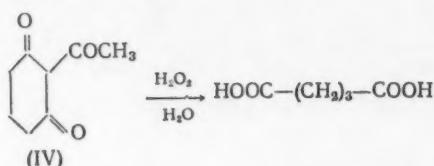
A more complex picture is found in the reaction of ethyl (2-oxocyclohexyl)glyoxylate (III) with hydrogen peroxide; this leads to a mixture of oxalic monoester, adipic acid, and a crystalline product of unestablished structure.

2,4-Pentanedione also reacts with hydrogen peroxide, but the peroxy compound isolated was found to be very explosive and was therefore not investigated further. In the treatment of malonic ester with hydrogen peroxide in alkaline medium at 20° for two hours only its hydrolysis product, malonic monoester, was obtained.

EXPERIMENTAL

Reaction of 1,3-cyclohexanedione with hydrogen peroxide. Addition was made of 15 ml of 30% hydrogen peroxide to 2.2 g of 1,3-cyclohexanedione in 20 ml of water at 25-30°. After five days at 20° evaporation of the mother solution yielded 1.3 g (50%) of glutaric acid, m.p. 95-96°.

Reaction of dimedon with hydrogen peroxide. Under analogous conditions from 2.8 g of dimedon we obtained 1.5 g (47%) of 3,3-dimethylglutaric acid, m.p. 90°.

Reaction of 2-oxocyclopentanecarboxaldehyde with hydrogen peroxide. In small portions, 2.9 g of 2-oxocyclopentanecarboxaldehyde (m.p. 71-73°) [9] was added under cooling with ice water to 15 ml of 30% hydrogen peroxide. Reaction proceeded with the evolution of much heat, and the temperature of the mixture rose to 90°. On cooling, 3.36 g (90%) of adipic acid, m.p. 149-151°, was precipitated.

Reaction of 2-oxocyclohexanecarboxaldehyde with hydrogen peroxide. Over a period of 20 minutes 12 ml of 30% hydrogen peroxide was added to 2.5 g of 2-oxocyclohexanecarboxaldehyde [b.p. 78-80° (8 mm); n_D^{20} 1.5120] [9]. Extraction with ether gave an oil, distillation of which gave 1 g (43.5%) of cyclopentanecarboxylic acid; b.p. 74-80° (2 mm); n_D^{21} 1.4529; m.p. 1-3°; amide m.p. 170-172°; it gave also 1.1 g (35%) of pimelic acid, b.p. 170-172° (2 mm) and m.p. 98-100°. For cyclopentanecarboxylic acid the literature gives m.p. from −3 to −1°; b.p. 104° (11 mm); n_D^{18} 1.4534 [4]; amide, m.p. 179° [10]; and for pimelic acid it gives m.p. 103° [11] and 105° [12]. The cyclopentanecarboxylic acid, its amide, and the pimelic acid that we obtained showed no depression of melting point in admixture with known samples.

Reaction of methyl derivatives of 2-oxocyclohexanecarboxaldehyde with hydrogen peroxide. Under the conditions of the preceding experiment we obtained the following results: 1) 4.65 g of 3-methyl-2-oxocyclohexanecarboxaldehyde [b.p. 85° (12 mm); $n_D^{25.5}$ 1.5010] [13] gave an oil, by the fractionation of which we isolated 2.2 g (52%) of 2-methylcyclopentanecarboxylic acid (b.p. 79-80° (2 mm); n_D^{21} 1.4514; amide, m.p. 150-152°) and 1.2 g (21%) of 2-methylpimelic acid (b.p. 170-173° (2 mm); dianilide, m.p. 163.5-165°). For trans-2-methylcyclopentanecarboxylic acid the literature [3] gives: b.p. 113° (13 mm); n_D^{22} 1.4504; amide, m.p. 147-148°. For 2-methylpimelic acid it gives [14]: b.p. 223-224° (15 mm); m.p. 59°; dianilide, m.p. 166-167°.

2) 4.8 g of 4-methyl-2-oxocyclohexanecarboxaldehyde [b.p. 70-72° (9 mm); n_D^{24} 1.4995] [13] gave 1.55 g (36%) of 3-methylcyclopentanecarboxylic acid [b.p. 89-91° (2 mm); n_D^{21} 1.4499; amide, m.p. 146-147°] and 2.25 g (59%) of 3-methylpimelic acid; b.p. 170-173° (2 mm); dianilide, m.p. 135-136°. For trans-3-methylcyclopentanecarboxylic acid the literature [15] gives: b.p. 115-116° (15 mm); n_D^{22} 1.4480; amide, m.p. 149-150°. For 3-methylpimelic acid it gives [4] m.p. 48-50°; dianilide, m.p. 136-137°.

3) 4.6 g of 5-methyl-2-oxocyclohexanecarboxaldehyde [b.p. 67-68° (8 mm); n_D^{25} 1.4990] [9] gave 1.25 g (30%) of 3-methylcyclopentanecarboxaylic acid [b.p. 91-93° (2 mm); $n_D^{27.5}$ 1.4445; amide, m.p. 145-146°] and 2.5 g (57%) of 4-methylpimelic acid; b.p. 182-184° (2 mm); m.p. 51-53°; dianilide, m.p. 157-158°. For 4-methylpimelic acid the literature [14] gives: m.p. 56-57°; dianilide, m.p. 158-159°.

Reaction of benzoylacetaldehyde with hydrogen peroxide. Over a period of 20 minutes 12 ml of 30% hydrogen peroxide was added to a solution of 2.8 g of benzoylacetaldehyde [16] and 2.24 g of potassium hydroxide in 20 ml of water at 25-30°. After acidification with dilute hydrochloric acid ether extraction gave 1 g (41%) of benzoic acid, m.p. 122-123°, undepressed by admixture of a known sample. By evaporation of the mother solution we isolated an unidentified oil.

Reaction of 2-acetyl-1,3-cyclohexanedione (IV) with hydrogen peroxide in an alkaline medium. Addition was made of 6 ml of 28% hydrogen peroxide to a solution of 1.54 g of 2-acetyl-1,3-cyclohexanedione (IV) [b.p. 81-83° (4 mm); m.p. 28-30°] [17] and 0.4 g of potassium hydroxide in 10 ml of water at 20°. At the end of the reaction we isolated 0.65 g (50%) of glutaric acid. By the reaction of 3 g of 2-acetyl-1,3-cyclohexanedione (IV) with hydrogen peroxide in absence of alkali, 1.9 g (76%) of glutaric acid was obtained.

Reaction of ethyl (2-oxocyclohexyl)glyoxylate (III) with hydrogen peroxide. In the course of one hour 40 ml of 30% hydrogen peroxide was added to 20 g of ethyl (2-oxocyclohexyl)glyoxylate [18] and 11.2 g of potassium hydroxide in 50 ml of water at 20-25°. After acidification with dilute hydrochloric acid, ether extraction gave 13.7 g of oil, the fractionation of which gave 6 g of oxalic monoester [b.p. 76-80° (2 mm); n_D^{18} 1.4490], which gave oxalic acid, m.p. 104-106°, on hydrolysis, and 0.5 g of adipic acid, m.p. 150-151°. After evaporation of the mother solution we obtained 2.2 g of a neutral solid, m.p. 90-92° (from aqueous alcohol), which was not investigated further.

Reaction of 2,4-pentanedione with hydrogen peroxide. Addition was made of 15 ml of 30% hydrogen peroxide to 2 g of 2,4-pentanedione at 25°. After ten days ether extraction gave 2.2 g of crystals, m.p. 103-104° (from benzene). The crystals were soluble in water, gave no reaction with ferric chloride, decolorized potassium permanganate solution, and exploded powerfully when heated rapidly or ground in a mortar. The peroxy compound was formed also when the reaction was carried out in presence of alkali.

SUMMARY

1. Under the action of hydrogen peroxide 1,3-cyclohexanedione and dimedon undergo oxidative cleavage to glutaric and 3,3-dimethylglutaric acids.

2. The oxidation of 2-oxocylopentanecarboxaldehyde with hydrogen peroxide in neutral and alkaline media leads to the formation of adipic acid. Under the same conditions 2-oxocyclohexanecarboxaldehydes give mixtures of pimelic and cyclopentanecarboxylic acids.

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FREE-RADICAL ADDITION OF CARBOXYLIC ACIDS
TO α-OLEFINS

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We have shown previously that at 135-200° in presence of t-butyl peroxide carboxylic acids and to α-olefins with formation of dialkylacetic acids [1]:

$$R-CH_2-COOH + CH_2=CH-R' \longrightarrow R'-CH_2CH_2CH-COOH$$
$$\underset{R}{|}$$
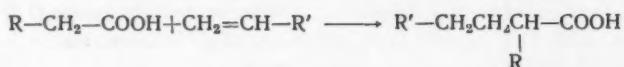
The methyl esters of the acids behave analogously with formation of methyl dialkylacetates.

In the present work we have made a more detailed investigation of the free-radical addition of carboxylic acids to α-olefins, and we examined the possibilities also of the synthesis both of trialkylacetic acids and of normal acids. The effect of the structures of the acid and olefin on their reactivity was elucidated, and the relation of the yield of addition products (1 : 1 adducts) to the reaction conditions, to the amount of t-butyl peroxide used, and to the molar ratio of acid: olefin was established. The conditions of individual experiments, the amounts of reactants and peroxide, the yields of 1 : 1 adducts, and the amounts of high-boiling products formed are given in Table 1. The properties of the 1 : 1 adducts obtained are shown in Table 2. We did not investigate the high-boiling products; they were probably telomer-homologs of various molecular weights. In all the experiments we isolated acetone and t-butyl alcohol, which were formed as a result of the breakdown of a t-butoxy radical and as a result of the abstraction by it of a hydrogen atom from the acid molecule; t-butyl alcohol was always obtained in the predominant amount, as compared to acetone. In most experiments the molar amounts of 1 : 1 adducts formed were more than twice as great as the molar amounts of peroxide used.

TABLE 1

Expt. No.	Reactants		Amt. taken for reaction (moles)			Temp. (°C)	Time (hr)	Yield of 1 : 1 adduct *		Residue (g)
	Acid	Olefin	acid	olefin	per-oxide			g	%	
1	CH₃CH₂COOH	1-Octene	2	0,2	0,05	136—140	5	27,2	73	8
2	(CH₃)₂CHCOOH	1-Decene	3	0,3	0,075	143—150	5	29	42,5	16
3	C₅H₁₁COOH	1-Decene	7	0,7	0,175	150—154	5	128	71	43
4	C₆H₁₃COOH	1-Nonene	7	0,7	0,175	150—155	5	124	69	45
5	C₆H₁₃COOH	4-Methyl-1-decene	6,5	0,65	0,16	160—163	6	120	65	44
6	C₆H₁₃COOH	5-Ethyl-1-nonene	5,48	0,71	0,187	151—157	7,5	123,5	61	56
7	C₆H₁₃COOH	2-Ethyl-1-hexene	4	0,4	0,1	160—164	5	32,5	33,5	22
8	C₇H₁₅COOH	1-Octene	5,9	0,59	0,15	150—155	5,5	100	66	46
9	CH₃COOC₆H₁₃	1-Decene	1,5	0,15	0,037	158—160	5	12	28	18
10	C₆H₁₃COOH	Fraction of b.p. 126-151°	5	92**	0,125	150—156	5	57	44	30

* Calculated on amount of olefin.

** In grams.

TABLE 2

Expt. No.	1 : 1 adduct	Mol. wt. found	Mol. wt. calc.	B. p. in °C (p in mm)	d_4^{20}	n_D^{50}	MR found	MR calc. °	found C	found H	calc. C	calc. H
1	$C_8H_{17}CHCOOH$ / CH_3	186,8	186,29	101—102 (0,5)	0,8959	1,4377	54,55	54,81				
2 *	$C_{10}H_{21}CCOOH$*** / CH_3	229,5	228,37	130—131 (1)								
3 *	$C_{10}H_{21}CHCOOH$ / C_4H_9	261,5	256,42	160—162 (1)	0,8821	1,4472	77,70	78,06				
4 *	$C_9H_{19}CHCOOH$ / C_5H_{11}	261,2	256,42	173—175 (1,5)	0,8809	1,4470	77,77	78,06				
5	$C_6H_{13}CH(CH_2)_3CHCOOH$ / CH_3 C_5H_{11}	285,2	284,47	160—162 (0,5)	0,8774	1,4500	87,13	87,35	76,16	12,71	75,99	12,76
6	$C_4H_9CH(CH_2)_4CHCOOH$ / C_2H_5 C_5H_{11}	284,5	284,47	158—162 (0,5)	0,8818	1,4518	87,00	87,35	76,15 75,83	12,82 12,86	75,99	12,76
7	$C_4H_9CHCH_2CHCOOH$ / C_2H_5 C_5H_{11}	245,4	242,40	128—130 (0,5)	0,8866	1,4473	73,09	73,41	75,73 74,32	12,78 12,39	74,32	12,48
8 *	$C_8H_{17}CHCOOH$ / C_6H_{13}	260,6	256,42	160—162 (0,1)	0,8817	1,4470	77,70	78,06	74,66	12,39	—	—
9 *	$C_{10}H_{21}CH_2COOC_6H_{13}$			118—119 (0,5)	0,8585	1,4402	87,36	87,50	76,02 76,04	12,67 12,89	75,99	12,76
10	Mixture of acids	282,2		137—147 (1)	0,8896	1,4480						
13—29 *	$C_{10}H_{21}—CH—COOH$ / C_5H_{11}	272,1	272,46	149—151 (1)	0,8789	1,4488	82,50	82,70	75,38 75,31	12,43 12,58	75,49	12,67

* Data in literature: 2) b.p. 184° (12 mm); m.p. 27° [2]; 3) b.p. 175-176° (3 mm); d_4^{25} 0,8789; n_D^{25} 1,4458 [3]; 4) b.p. 178-179° (3 mm); d_4^{25} 0,8887; n_D^{25} 1,4518 [3]; 8) b.p. 165-168° (2 mm); d_4^{25} 0,8768; n_D^{25} 1,4495 [3]; 9) n_D^{20} 1,4382 [4]; 13-29) b.p. 177-182° (2-3 mm) [5].

** The molecular weight was determined from acid values.

*** m.p. 26-27°.

On the basis of general theoretical considerations and our results, the mechanism of the addition of acids to olefins is most probably expressed by the following series of equations:

$$(CH_3)_3COOC(CH_3)_3 \longrightarrow 2(CH_3)CO^\bullet$$
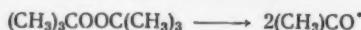
Part of the t-butoxy radicals decompose:

$$(CH_3)_3CO^\bullet \longrightarrow CH_3^\bullet + CH_3COCH_3$$

$$R-CH_2COOH + (CH_3)_3CO^\bullet \longrightarrow R-\overset{\bullet}{C}HCOOH + (CH_3)_3COH$$

$$R-\overset{\bullet}{C}H-COOH + CH_2=CH-R' \longrightarrow R'-\overset{\bullet}{C}H-CH_2-\underset{\underset{R}{|}}{C}H-COOH$$

$$R'-\underset{\underset{R}{|}}{C}HCH_2CH-COOH + R-CH_2COOH \longrightarrow R'-CH_2CH_2\underset{\underset{R}{|}}{C}H-COOH + R-\overset{\bullet}{C}HCOOH$$
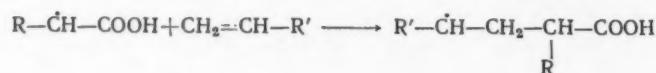
At stage (d) the propagation of the chain occurs with formation of the 1 : 1 adduct and a new radical, which continues the chain. The radical formed at stage (c) may combine with another or several more olefin molecules, which leads to the formation of telomerization products. In carrying out the reaction we strove to create conditions such that the amount of telomers formed would be at a minimum, thus ensuring a maximum yield of the 1 : 1 adduct. This requirement was fulfilled largely as a result of the constant large excess of acid over olefin in the reaction zone and as a result of the high reaction temperature (above 140°). The reaction was carried out in a glass apparatus at atmospheric pressure. The procedure was the same in all experiments: a solution of t-butyl peroxide and the olefin in one-third the total calculated amount of acid was added dropwise at a regular rate to the remainder of the acid over the period of time stated in Table 1 (5-7 hours).

TABLE 3.

Expt. No.	Reactants		Amt. taken for reaction (moles)			Temp. (°C)		Yield of 1 : 1 adduct*	
	acid	α-olefin	acid	α-olefin	per-oxide			g	%
11	CH_3CH_2COOH	1-Octene	5	0,225	0,056	159—162	6	19,2	46,5
	C_5H_{11}CH_2COOH		5					15	27,5
12	C_2H_5CH_2COOH	1-Octene	4	0,2	0,05	158—164	6	14	35
	C_6H_{13}CH_2COOH		4					18	35

* Calculated on amount of 1-octene.

At molar proportions of acid : olefin : peroxide of 10 : 1 : 0.25, propionic, hexanoic, heptanoic, and octanoic acids form 1 : 1 adducts in about 70% yield with normal C_8-C_{10} α-olefins (Experiments 1, 3, 4, and 8). On the basis of the results obtained in the present and previous [1] investigations, it may be considered that the chain length of the normal α-olefin studied (C_6-C_{13}) has no effect on the yield of 1 : 1 adduct. Branched α-olefins in which the branching is not at the double bond give 1 : 1 adducts in the same yields as α-olefins of normal structure (Experiments 5 and 6). Olefins having a branching at the double bond are less reactive than normal α-olefins. Thus, in the reaction of 2-ethyl-1-hexene with heptanoic acid the 1 : 1 adduct (4-ethyl-2-pentylnonanoic acid) was obtained in 33.5% yield, part of the olefin (about 15%) remaining unchanged (Experiment 7):

TABLE 4

Expt. No.	1 : 1 Adduct	Mol. wt. found	Mol. wt. calc.	B.p. in °C ($\underline{p}$ in mm)	d_4^{20}	n_D^{20}	MR found	MR calc.	found C	found H	calculated C	calculated H
	$C_8H_{17}-CH-COOH$ $\quad\quad\;\; CH_3$	189,0	186,29	128—130 (1,0)	0,8975	1,4388	54,50	54,81	70,77 70,50	11,85 11,64	70,92	11,90
11*	$C_8H_{17}-CH-COOH$ $\quad\quad\;\; C_5H_{11}$			138—140 (0,5)	0,8822	1,4450	73,13	73,41	74,55 74,51	12,44 12,37	74,32	12,48
12*	$C_8H_{17}-CH-COOH$ $\quad\quad\;\; C_2H_5$	202,8	200,31	105—108 (0,5)	0,8932	1,4400	59,11	59,46	71,82 71,65	11,87 11,79	71,94	12,06
	$C_8H_{17}-CH-COOH$ $\quad\quad\;\; C_6H_{13}$			136—138 (0,5)	0,8800	1,4468	77,82	78,06	74,76 74,66	12,49 12,48	74,94	12,58

*Data in the literature: octylpentylacetic acid, b.p. 161-164° (2-3 mm) [5]; ethyloctylacetic acid, b.p. 186° (12 mm) [6]; hexyloctylacetic acid, see Table 2.

** The molecular weight was determined from acid values.

$$C_5H_{11}CH_2COOH + CH_2=\underset{\underset{C_2H_5}{|}}{C}-C_4H_9 \longrightarrow C_4H_9-\underset{\underset{C_2H_5}{|}}{CH}-CH_2\underset{\underset{C_5H_{11}}{|}}{CH}-COOH$$
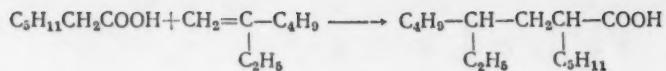
In the reaction with acids, not only individual olefins can be used, but also mixtures of them. We brought about the addition of heptanoic acid to olefins obtained by the pyrolysis of paraffin. In the reaction we took the fraction of b.p. 126-151°, which consisted mainly of C_9 alkenes, the content of unsaturated hydrocarbons being 68% according to the bromine value. As a result we obtained a mixture of acids in 45% yield, calculated on nonene (Expt. 10).

TABLE 5. Reaction of Heptanoic Acid (A) with 1-Decene (B)

Expt. No.	Amt. taken for reaction (moles)			Temp. (°C)	Time (hr)	Yield of 1:1 adduct		Residue (g)	Acid value of residue
	A	B	peroxide						
13	1,5	0,15	0,038	119—121	5	5,5	13,5	6,7	578,5
14	1,5	0,15	0,038	129—131	5	12,3	30,4	8,2	543
15	1,5	0,15	0,038	140—142	5	26,6	65,5	10,8	434
16	1,5	0,15	0,038	158—162	5	26,3	65	9,8	405
17	1,5	0,15	0,038	198—202	5	26	64	8,9	375
18	1,5	0,15	0,038	155—161	1/4	20,6	50,7	15,4	431
19	1,5	0,15	0,038	159—161	1	25,6	63	12,6	413,5
20	1,5	0,15	0,038	159—161	3	26,6	65,5	10,7	363
21	1,5	0,15	0,038	158—163	10	28,7	70,8	9,1	364,5
22	0,375	0,15	0,038	155—160	5	12,9	31,8	15,5	550
23	0,75	0,15	0,038	157—160	5	19	47,2	13,7	477
24	3	0,15	0,038	158—163	5	32,2	79,5	8	325
25	6	0,15	0,038	158—162	5	33,5	82,5	4,5	254
26	1,5	0,15	0,0075	158—162	5	9,2	22,6	6,2	505
27	1,5	0,15	0,015	155—162	5	16,7	41,2	8,2	—
28	1,5	0,15	0,0225	158—161	5	21,9	54	8,8	438
29	1,5	0,15	0,075	158—163	5	27,6	68,2	11,5	370

In the series of normal carboxylic acids, propionic was found to be the most reactive toward α-olefins. Acids of higher molecular weight have about equal reactivities, which are considerably less than that of propionic acid. For the quantitative estimation of the reactivities of the acids, competing reactions of the simultaneous addition of propionic and heptanoic acids to 1-octene were carried out, and also competing simultaneous additions of butyric and octanoic acids to 1-octene. The reaction conditions and the yields of 1 : 1 adducts are given in Table 3, and the properties of the dialkylacetic acids then obtained are given in Table 4. A considerable difference in the yields of 1 : 1 adducts was observed only for the first pair of acids: from propionic acid methyloctylacetic acid was obtained in 46.5% yield and, from heptanoic acid octylpentylacetic acid was obtained in 27.5% yield. In the experiment with butyric and octanoic acids the adducts were obtained in identical yields of 35%.

On carrying out the addition of isobutyric acid to 1-decene (Expt. 2) we obtained the 1 : 1 adduct in a lower yield than that obtained with normal acids, which is probably to be explained by steric factors.

$$C_8H_{17}CH=CH_2 + (CH_3)_2CHCOOH \longrightarrow C_{10}H_{21}-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-COOH$$
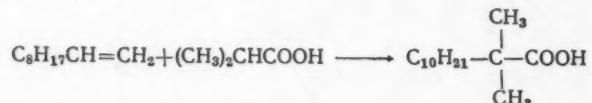
Acids not containing an α-C—H bond are in general incapable of addition to α-olefins under our conditions. Thus, we did not succeed in obtaining the adduct from trimethylacetic acid and 1-heptene and that from ethyldimethylacetic acid and 1-decene. These reactions were attempted at 142-158° with molar proportions of acid : olefin : peroxide of 1.5 : 0.15 : 0.038. We obtained as a result only small amounts (2-3 g) of wide-boiling fractions, which, judging from the results of titration, contained substances containing the carboxy group.

It has already been noted that methyl heptanoate and methyl hexanoate add to α-olefins just as readily as the free acids. However, we were unable to bring about the addition of methyl acetate to 1-decene [1]. The low boiling point of methyl acetate did not allow us to carry out the reaction in glass at atmospheric pressure, and the experiments were therefore carried out in an autoclave; the peroxide and the olefin were added to the ester in three portions. Under similar conditions methyl propionate, butyrate, and isobutyrate formed 1 : 1 adducts in 25-35% yield. As would be expected, the hydrogen atom of the methyl group of acetic acid or its ester is considerably less readily abstracted by peroxide radicals than the hydrogen atom of α-CH_2 in acids of higher molecular weight. Nevertheless, in the present work we succeeded in adding an acetic ester to an olefin. For this purpose we took hexyl acetate, because its boiling point permitted reaction by the usual procedure. In its reaction with 1-decene we obtained hexyl laurate in 28% yield (Expt. 9):

$$CH_3COOC_6H_{13}+CH_2=CH-C_8H_{17} \longrightarrow C_{10}H_{21}CH_2COOC_6H_{13}$$
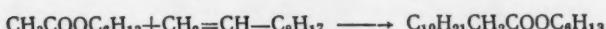
Fig. 1. Relation of yield of decylpentylacetic acid to reaction temperature. Conditions: molar proportions of acid : olefin : peroxide of 10 : 1 : 0.25; duration of experiments five hours.
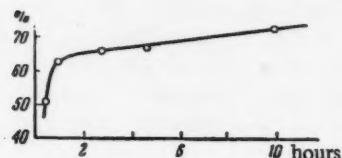
Fig. 2. Relation of yield of decylpentylacetic acid to the duration of experiment. Conditions: molar proportions of acid : olefin : peroxide of 10 : 1 : 0.25; reaction temperature 157-163°.

Only extremely small amounts of hexyl acetate added to 1-decene by reaction at the hexyl group. Hence, with respect to their reactivity in the formation of 1 : 1 adducts with α-olefins the acids investigated fall into the following series: CH_3CH_2COOH > $R-CH_2CH_2COOH$ > > $(CH_3)_2CHCOOH$ > CH_3COOH.

When benzoyl peroxide was used as initiator in the reaction of heptanoic acid with 1-decene, the 1 : 1 adduct was obtained in a yield of only 15%. The reaction was carried out at 160-165° with proportions of acid : olefin : peroxide of 10 : 1 : 0.25. The peroxide was added over a period of five hours in nine equal portions at approximately equal intervals. When 2,2'-azobisisobutyronitrile was used under similar conditions, we did not succeed in obtaining any 1 : 1 adduct.

In a series of experiments for the case of the addition of heptanoic acid to 1-decene (Table 5) we studied the effect of the reaction conditions (temperature and time of addition of the olefin and peroxide to the acid), the molar ratio of acid : olefin, and the amount of peroxide used on the yield of decylpentylacetic acid (the properties of this are given in Table 2). Figure 1 shows the relation of yield on temperature for constant proportions of acid : olefin : peroxide of 10 : 1 : 0.25 and for a reaction time of five hours. At 120° and 130° decylpentylacetic acid is obtained in low yield. The yield rises sharply (from 30.4% to 65.5%) with rise in temperature to 140°, and it remains almost constant with further rise in temperature to 200°.

Figure 2 expresses the relation of the yield of the 1 : 1 adduct to the rate of addition of the peroxide and olefin to the acid. Increase in the duration of the reaction from one hour to ten does not greatly increase the yield, which is appreciably reduced at a reaction time of 15 minutes. However, even after that time the 1 : 1 adduct is obtained in 50% yield. In this case the largest amount of high-boiling residue is formed.

Figure 3 shows how the yield of the 1 : 1 adduct changes with change in the ratio of acid : olefin from 2.5 : 1 to 40 : 1. With ratios of 10 : 1 and 20 : 1 the amounts of the acid formed were 65% and 79.5% respectively. Lowering of the ratio led to a sharp fall in the yield. Figure 4 gives the relation of the yield of decylpentylacetic acid to the amount of peroxide used, calculated on the olefin and on the peroxide. With a ratio of acid : olefin of 10 : 1 it is most rational to used 25% of the peroxide with respect to the olefin.

Thus, the optimum conditions are the following: temperature 140-160°; duration of reaction 3-5 hours; molar proportions of acid : olefin : peroxide of 10 : 1 : 0.25. Under these conditions the yield of the 1 : 1 adduct is 60-70%. The method of synthesizing dialkylacetic acids that we have developed is simpler and more convenient than the malonic synthesis that is often used for this purpose, and it may compete successfully with the latter in the preparation of dialkylacetic acids in which one of the alkyl groups contains not less than five carbon atoms.
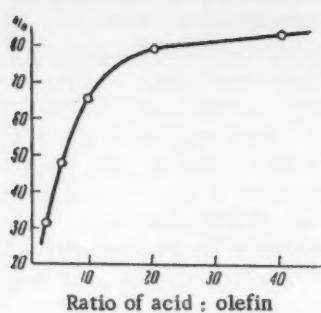
Fig. 3. Relation of the yield of decyl-pentylacetic acid to the molar ratio of acid : olefin. Conditions: molar ratio of olefin : peroxide of 1 : 0.25; duration of experiments five hours; reaction temperature 157-164°.
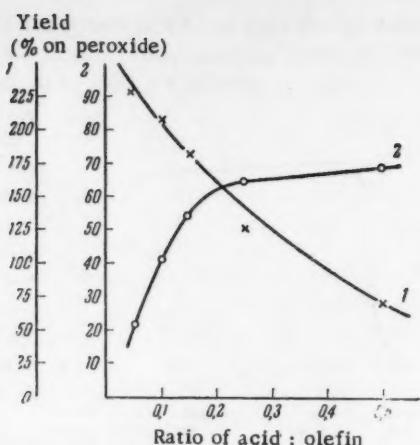

Fig. 4. Relation of the yield of decylpentylacetic acid to the molar ratio of peroxide : olefin. Conditions: molar ratio of acid : olefin of 10 : 1; reaction temperature 158-163°; duration of experiments five hours.

EXPERIMENTAL

Olefins. 1-Octene, 1-nonene, 1-decene, and 2-ethyl-1-hexene were prepared by the pyrolysis of the corresponding acetates. 4-Methyl-1-decene and 5-ethyl-1-nonene were prepared by the Grignard-Wurtz reaction from allyl bromide with 2-bromooctane and 1-bromo-2-ethylhexane respectively. In Expt. 10 we used a fraction of b.p. 126-151°; d_4^{20} 0.7413; n_D^{20} 1.4188, and bromine value 86.5, which was isolated by straight distillation from the thermal-cracking products from synthetic paraffin at Khimkombinat in Novocherkassk. The content of unsaturated hydrocarbons in this fraction (calculated as nonene) was 68%, and as well as α-olefins olefins with the double bond in another position were also present.

Addition of acids to α-olefins (Experiments 1-29). Two-thirds of the total calculated amount of acid (hexyl acetate in Expt. 9) was placed in a four-necked flask fitted with stirrer, condenser, calibrated dropping funnel, and thermometer. When the acid had been heated to the required temperature, uniform dropwise addition was made with stirring of a solution of the peroxide and olefin in the remaining one-third of the acid. In Experiments 11 and 12, to a mixture of the two acids a solution of 1-octene and a mixture of the same acids was added. In all experiments, when the addition of the solution was complete the reaction mixture was heated for one hour further at the same temperature. Acetone, t-butyl alcohol, and excess of acid were then distilled off. In Expt. 7 we isolated 7 g of unchanged 2-ethyl-1-hexene; in Expt. 10, 54 g of hydrocarbons containing unsaturateds (bromine value about 16.5%) was isolated. In the remaining experiments the olefins reacted completely. From the high-boiling reaction products the 1 : 1 adducts were isolated by fractional distillation; their yields were usually determined after redistillation. The amounts of substances boiling higher than the 1 : 1 adducts are shown for each experiment in Tables 1, 3, and 5 in the column marked "Residue." The acids obtained in Expts. 5, 6, 7, and 10, and also octylpentylacetic and heptyloctylacetic acids obtained in Expts. 11 and 12, were purified chromatographically from possible impurities on a column of 150-200 mesh ASK silica gel. Such impurities could be products of the telomerization and polymerization of the olefins, and also dicarboxylic acids formed by the dimerization of R−ĊHCOOH radicals. The amounts of impurities were very small and could be removed easily by passing the 1 : 1 adducts through a silica gel column. Thus, before purification 6-methyl-2-pentyldodecanoic acid (Expt. 5) had d_4^{20} 0.8783; n_D^{20} 1.4501, and mol. wt. (calculated from the acid value) 289.2; after purification it had d_4^{20} 0.8774; n_D^{20} 1.4500, and mol. wt. 285.2.

To prove the structure of the 1 : 1 adducts obtained Expt. 9, 3.4 g of this product was heated with 20 ml of liquid ammonia at 150-160° for ten hours in a 150 ml autoclave. From the resulting crystalline mass we isolated 2.4 g of lauramide, m.p. 103° (the literature gives 100° [7] and 102° [8]) and 0.1 g of crystals, m.p. 77-78.5°, similar in appearance to acetamide crystals. For acetamide m.p. 81°.

SUMMARY

1. A preparative method was developed for the synthesis of dialkylacetic acids by the addition of acids of normal structure to α-olefins.

2. A study was made of the reactivities of acids of different molecular weight and structure and of different α-olefins in this reaction.

3. The relation was determined of the yields of 1 : 1 adducts to the reaction temperature and time, the amount of t-butyl peroxide used, and the molar ratio of acid : olefin.

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SYNTHESIS OF ETHOXYACETALDEHYDE,
AND ITS CHEMICAL REACTIONS

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In an investigation of the dehydrogenation of alcohols over various catalysts we decided to study the dehydrogenation of 2-ethoxyethanol. The catalytic dehydrogenation of 2-ethoxyethanol over a catalyst prepared by the reduction of cupric oxide [1-4], and also over a copper-silicon alloy [5], has been described several times in the literature. However, in these experiments neither the conversion nor the yield of ethoxyacetaldehyde exceeded 20-30%. Later investigations [6] showed that even these results were not reproducible, and the yield of ethoxyacetaldehyde did not exceed 10-15%.

After a study of the catalytic dehydrogenation of 2-ethoxyethanol and also of its aqueous solutions over various catalysts (reduced cupric oxide, brass, copper rings, copper-silicon alloy, etc.) we came to the conclusion that it is impossible to obtain satisfactory results in this way, as it is always mainly cleavage of the 2-thoxyethanol that occurs, and the final products are gases, acetaldehyde, and only traces of ethoxyacetaldehyde. We therefore went over to a study of the dehydrogenation of 2-thoxyethanol over metal catalysts in a stream of air. No information about such investigations was found in the literature, and we carried out much work in order to select the conditions required in this reaction. The results obtained are given in part in the table.

We succeeded in increasing the yield of ethoxyacetaldehyde to 60-65%. The best conditions for the dehydrogenation were found to be: pressure 300-400 mm, temperature 600°, and catalyst in the form of silver triangles.

Ethoxyacetaldehyde, which had now become accessible, is an extremely reactive compound which rapidly polymerizes on standing; however, like formaldehyde solutions, its solutions in water and alcohols do not change. In the study of the chemical properties of ethoxyacetaldehyde, we therefore decided to use its azeotrope with water, which is stable to keeping. Our experiments showed that many reactions take place with the azeotrope with the same yields as those obtained with pure ethoxyacetaldehyde. In studying the chemical behavior of this little-studied aldehyde, we examined it in various reactions, which may be represented as follows:

$$C_2H_5OCH=CHOC_2H_5 \quad (IV)$$

$$C_2H_5OCH_2CH(OC_2H_5)_2 \longrightarrow C_2H_5OCH_2-CH \begin{smallmatrix} OC_2H_5 \\ OCOCH_3 \end{smallmatrix} \quad (III)$$
(II)

$$C_2H_5OCH_2CH_2OH \longrightarrow C_2H_5OCH_2CHO \longrightarrow C_2H_5OCH=CHOCOCH_3 \quad (V)$$
(I)

$$C_2H_5OCH_2CH \begin{smallmatrix} OH \\ CN \end{smallmatrix} \qquad C_2H_5OCH_2CH(OH)-C\equiv CCH_2OH \quad (VII)$$
(VI)
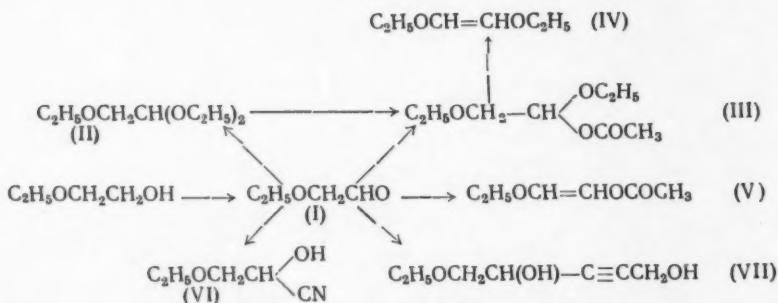
Ethoxyacetaldehyde (I), and also its azeotrope, is readily converted into its diethyl acetal (II), which, on being heated with acetic anhydride in presence of p-toluenesulfonic acid, is converted into the acylal (III), which at 160° loses a molecule of acetic acid and is converted into 1,2-diethoxyethylene (IV). When ethoxyacetaldehyde is boiled for a long time with acetic anhydride and a little potassium acetate, 2-ethoxyvinyl acetate (V) is formed in a yield of about 20%.

Air Oxidation of 2-Ethoxyethanol Diluted with Water in the Proportions of 1 Mole of 2-Ethoxyethanol to 1.5 Moles of Water

Catalyst	Temp. (°C)	Amt. of ethoxythanol taken (moles)	Time (min)	Oxygen (% of theor. amt)	Yield of aldehyde (moles)	Conversion of alcohol
Copper triangles, silvered; same size as silver ones	545	2,300	159	218	0,840	
ditto	500	1,140	43	115	0,373	67,5
» »	500	1,080	40	180	0,490	89
» »	470	0,366	15,5	217	0,142	
» »	490	0,390	19,5	127	0,156	
Fine copper turnings, silvered	535	2,660	178	158	1,060	
ditto	550	0,940	40	80	0,250	
Pumice, silvered	600	0,486	21,5	98	0,104	
Silver triangles						
ditto	565	0,662	32,5	143	0,270	
» »	530	0,365	17	90	0,165	
» »	520	0,945	69	83	0,384	74
				Air diluted with nitrogen 4,5-fold		
» »	600	0,637	29	130	0,388	
				Vacuum 345 mm		
» »*	600	0,62	27	135	0,386	
				Vacuum 210 mm		
» »*	600	1,07	19	131	0,61	90
				Vacuum 530 mm		

* Without water.

On reaction of ethoxyacetaldehyde, or its azeotrope, with acetone cyanohydrin in presence of potassium carbonate, 3-ethoxy-2-hydroxypropionitrile is formed in 60% yield. Ethoxyacetaldehyde also condenses smoothly with 2-propyn-1-ol in presence of cuprous oxide. The acetylenic glycol (VII) is then formed in a yield of about 60%.

We studied also the reaction between the chloro ether (VIII) (which was prepared from ethoxyacetaldehyde, ethanol, and hydrogen chloride) and potassium acetate. We isolated the acylal (III) in low yield, and we obtained also some of the diethyl acetal (II), formed probably by the disproportionation of the unsymmetrical acylal (III).

Hydrolysis of the acetal (II), and also of 2-thoxyvinyl acetate (V) and the unsymmetrical acylal (III), in presence of hydroxylamine gave rather high values for the carbonyl content of the molecule, so that this method is not suitable for analytical purposes in this case. It is interesting to note that in the hydrolysis of acetals [7] in presence of 2,4-dinitrophenylhydrazine the glyoxal hydrazone is formed as well as the hydrazone of ethoxyacetaldehyde, i.e., the hydrazine is consumed not only in the formation of the hydrazone, but also in the oxidation of ethoxyacetaldehyde to glyoxal.

EXPERIMENTAL

Preparation of ethoxyacetaldehyde. Ethoxyacetaldehyde was prepared by the dehydrogenation of 2-ethoxyethanol (b.p. 134-135°; n_D^{20} 1.4075) over various catalysts in a quartz reactor, which is shown diagrammatically in figure. After a series of experiments had been carried out (see table) it was found that the best method for the preparation of ethoxyacetaldehyde was the dehydrogenation of 2-ethoxyethanol in a vacuum over a catalyst consisting of silver triangles having sides of length 1.5 mm, which were prepared from wire of diameter 0.3 mm (silver content 99.99%). After long use the catalyst fell appreciably in activity, but it could be regenerated by the passage of air at about 400°.

A mixture of 57.3 g of 2-ethoxyethanol (0.637 mole) and 17.2 g of water (0.955 mole) was passed into an evaporator, in which the vapor was mixed with air. The liquid was fed at such a rate that there was no accumulation of condensate in the evaporator. The amount of air fed in was 45 liters (130% of the theoretical amount). The mixture of vapor and air was passed through the reactor, which contained 15 ml of silver triangles as catalyst. The process was carried out at 600° and 345 mm for 30 minutes. The resulting condensate was fractionated through a

column of 20 plate efficiency. We obtained 44.5 ml of a mixture of ethoxyacetaldehyde and water in the form of an azeotrope of b.p. 90-91° and n^{18} 1.4236 (the literature [2, 4] gives b.p. 90-91°), and according to analysis this contained 0.388 mole of ethoxyacetaldehyde. The yield of ethoxyacetaldehyde was thus 61%.

Azeotrope (b.p. 90-91°) from a series of experiments (158 ml in all) and 150 ml of benzene were boiled together in an apparatus with a water separator until the separation of water ceased. Xylene (60 ml) was then added to the reaction mixture as a carrier liquid, and the mixture was fractionated through the 20-plate column. We then obtained 77 g of ethoxyacetaldehyde, b.p. 103-105° and $n_D^{22.5}$ 1.3935, i.e., 67% of the amount present in the azeotrope. The literature [2, 4] gives 104-106°. The residue consisted of ethoxyacetaldehyde polymers, which were depolymerized to the monomer on being heated with 0.1% of p-toluenesulfonic acid. The yield of ethoxyacetaldehyde obtained by the depolymerization of its polymers was 50%. Pure ethoxyacetaldehyde polymerizes fairly rapidly on standing, but its solutions in water or alcohol are stable.

← Air

2-Ethoxyethanol

Metal bath

Catalyst

Condenser

→ To trap and pump

Apparatus for the preparation of ethoxy-acetaldehyde (one-half true size).

Preparation of ethoxyacetaldehyde diethyl acetal (II). a) With stirring, 62.4 g (1.36 moles) of absolute alcohol containing 1% of hydrogen chloride was added gradually to 29.5 g (0.33 mole) of ethoxyacetaldehyde (I) cooled with a mixture of ice and salt. The mixture was left at room temperature for 44 hours and then neutralized by adding dry sodium carbonate with stirring; it was poured into an equal volume of concentrated sodium carbonate solution. The reaction product was extracted with three 35 ml portions of ether, and the ether extract was dried over potassium carbonate. Ether was distilled off, and distillation of the residue through a column gave 34 g (72%) of ethoxyacetaldehyde diethyl acetal (II); b.p. 52.5-54° (8 mm); n_D^{21} 1.4040. The literature [7, 8] gives: b.p. 164-165°; n_D^{25} 1.3889.

b) A mixture of 234 g of ethanol, 0.13 g of p-toluenesulfonic acid, and 290 ml of benzene was added to 91 g of the aqueous azeotrope of ethoxyacetaldehyde (b.p. 90-91°) containing 72 g of the aldehyde. The mixture was boiled with a water separator until water ceased to separate (four days). The reaction product was fractionated through a column of 20 plate efficiency (20 ml of decalin was added as carrier liquid). This gave 67 g of ethoxy-acetaldehyde diethyl acetal (II), b.p. 165-167°; $n_D^{24.5}$ 1.3990.

Synthesis of 2-ethoxyvinyl acetate (V). A mixture was 49 g of anhydrous ethoxyacetaldehyde, 148 g of acetic anhydride, and 8.75 g of potassium acetate was refluxed for one hour. The reaction mixture was washed six times with ice water, and then three times with 5% sodium carbonate solution. The reaction product was extracted with ether and fractionated through the 20 plate column. We then obtained 13 g of 2-ethoxyvinyl acetate (V); b.p. 86.5-88° (38 mm); $n_D^{23.5}$ 1.4358. Found: C 54.60, 54.71; H 7.7, 7.54%. $C_6H_{10}O_3$. Calculated: C 55.38; H 7.66%. The molecular weight, determined cryoscopically in benzene, was 130.9 (calculated 130). The substance decolorized bromine water.

3-Ethoxy-2-hydroxypropionitrile (VI). A mixture of 20 g of the azeotrope of ethoxyacetaldehyde (0.266 mole), 47.6 g (0.54 mole) of acetone cyanohydrin, and 18 ml of catalyst (concentrated methanolic potassium carbonate) was left overnight at room temperature. The reaction mixture was acidified with concentrated sulfuric acid, methanol and acetone was distilled off, a further 60 ml of methanolic potassium carbonate was added, and the reaction mixture was left further for 12 hours at room temperature. After analogous treatment of the reaction products and vacuum fractionation of the residue (after removal of solvents), we obtained 17.5 g (57%) of ethoxyacetaldehyde cyanohydrin (3-ethoxy-2-hydroxypropionitrile) (VI); b.p. 112-113° (14 mm); $n_D^{25.5}$ 1.4250. Found: C 52.00, 51.81; H 7.77, 7.89%. $C_5H_9O_2N$. Calculated: C 52.16; H 7.83%.

Condensation of ethoxyacetaldehyde with 2-propyn-1-ol. A mixture of 61.3 g of 2-propyn-1-ol, 174.8 g of the aqueous azeotrope of ethoxyacetaldehyde, 74 ml of water, 0.8 g of calcium carbonate, and catalyst (prepared by the precipitation of cuprous oxide from a solution of 12 g of cuprous chloride in 180 ml of 18% hydrochloric acid with 180 ml of 40% potassium hydroxide) was stirred in a nitrogen atmosphere at 100° for 42 hours. After removal

of catalyst, the filtrate combined with 400 ml of ethanol (washings) was evaporated, and the residue was vacuum-distilled. This gave 67 g (62%) of 5-ethoxy-2-pentyne-1,4-diol (VII); b.p. 121-122° (1 mm); $n_D^{22.5}$ 1.4791. Found: C 58.48, 58.67; H 8.32, 8.35%. $C_7H_{12}O_3$. Calculated: C 58.33; H 8.33%.

Reaction of ethoxyacetaldehyde diethyl acetal with acetic anhydride. A mixture of 32.6 g of the acetal (II), 20.5 g of acetic anhydride, and 0.2 g of p-toluenesulfonic acid was refluxed for six hours. After the removal of ethyl acetate the residue was vacuum-distilled through a column, which gave 7.4 g of ethoxyacetaldehyde diethyl acetal and 12.4 g (50%) of the acylal 1,2-diethoxyethyl acetate (III); b.p. 78-81° (14 mm); $n_D^{21.5}$ 1.4077. After redistillation (III) had: b.p. 80-80.5° (13.5 mm); $n_D^{19.5}$ 1.4082. Found: C 54.54, 54.61; H 8.97, 9.1%. $C_8H_{16}O_4$. Calculated: C 54.54; H 9.09%.

Preparation of 1,2-diethoxyethylene (IV). The acylal (III) (59.3 g) was refluxed for two hours, after which the mixture was distilled very slowly from a flask fitted with a long column. The reaction product was washed twice with 20% sodium carbonate solution, dried over potassium carbonate, and finally fractionated over potassium hydroxide. The fraction of b.p. 132-159° then obtained was fractionated through a column. This gave 21.15 g (32%) of 1,2-diethoxyethylene; b.p. 131-133°; $n_D^{19.5}$ 1.4218. The literature [7, 8] gives: b.p. 131-134°; n_D^{25} 1.4205.

Reaction of 1-chloro-2-ethoxyethyl ethyl ether (VIII) with potassium acetate. The chloro ether (VIII) (0.56 mole) was prepared in accordance with [4] and added to 55 g (0.56 mole) of potassium acetate contained in a flask fitted with a stirrer and a calcium chloride tube; the reaction mixture was then left overnight at room temperature. On the next day the reaction product was stirred further for two hours at 100°, cooled, and diluted with 50 ml of ether. After removal of ether, the residue was vacuum-distilled through a column. We then isolated 8 g of ethoxyacetaldehyde diethyl acetal (II), b.p. 64.5-68.5° (15 mm) and n_D^{24} 1.4004, and 4 g of the acylal (III), b.p. 80.7-85° (15 mm) and n_D^{23} 1.4150.

SUMMARY

1. A convenient method for the synthesis of ethoxyacetaldehyde was developed.

2. Ethoxyacetaldehyde readily undergoes the usual reactions of aldehydes. Some of its acetals, its cyanohydrin, and the product of its condensation with 2-propyn-1-ol were prepared for the first time.

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CELLULOSE AND CHITIN ESTERS, AND THE REACTIVITY
OF CELLULOSE AND CHITIN

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Unlike other polysaccharides, cellulose and chitin have highly regular molecular structures and strongly marked stereospecificity; they belong to the β-series of sugars with a 1,4-link between the β-glucose units. These polysaccharides differ in that the chitin molecule contains an acetamide grouping at $NHCOCH_3$ of the glucose residue, instead of hydroxyl. Both polysaccharides give sharp x-ray diagrams [1, 2]; the infrared spectra indicate the presence of hydrogen bonds both in cellulose [3] and in chitin [4]. The way in which cellulose, this strictly linear macromolecular substance, is formed in the cells of plants has not yet been elucidated; it is not clear what enzymes and conditions determine the formation in the plant of regularly constructed cellulose or irregularly constructed starch. There is still less information on the way in which chitin is formed. Only one thing is clear: no transformation from cellulose into chitin occurs in nature.

It is very difficult to aminate cellulose; many chemists have tried to do this, for example by the action of ammonia on cellulose tosyl esters [5]. In our laboratory attempts have been made to aminate cellulose via the mesyl (methanesulfonic) esters of cellulose [6]. By the action of ammonia on cellulose mesyl esters a low (2.5-4% N) degree of amination was achieved. It is sufficient to have a low amino content in cellulose for the fiber to dye with wool dyes. Our experiments showed that the addition of chitin to cellulose fibers ensures their good dyeability with wool dyes.

Very few derivatives of chitin have been described, which contrasts with the case of cellulose, in whose chain many transformations have been made with the formation of ethers and esters, some of which, e.g., cellulose nitrate, cellulose acetate, and ethylcellulose, are manufactured both here and abroad in enormous quantities. Syntheses of chitin derivatives have not yet passed out of the sphere of laboratory experiments and are few in number. This is to be explained by the fact that chitin is of low reactivity. The cause of this probably lies in the disposition and packing of the molecules of chitin, and only partly in the effect of the presence of the acetamido group in changing the behavior of chitin to swelling and dissolution, as compared with that of cellulose.

Unlike cellulose, chitin does not dissolve in cuprammonium solution, in the cadmium-ethylenediamine complex, in the sodium iron tartrate complex, and in quaternary ammonium hydroxides. The behavior of chitin toward good solvents for cellulose suggests the conclusion that the solubility of cellulose in these solvents is to be attributed to the presence in the cellulose molecule of two neighboring hydroxyls, which are responsible for the formation of molecular compounds with complexes, in accordance with the investigations of Danilov and Okun' on the behavior of cellulose toward cuprammonium complexes [7]. Chitin dissolves fairly well in phosphoric and nitric acids, and films may be formed from its concentrated solutions [8]. Chitin dissolves in phosphoric acid at phosphoric acid concentrations of 78.4-97.2% [8], but cellulose [9] dissolves in phosphoric acid within two concentration ranges, 82-84% and 92-97%, corresponding to the monohydrate $H_3PO_4 \cdot H_2O$ (84.4% of acid) and the semihydrate $2H_3PO_4 \cdot H_2O$ (91.6% of acid), in accord with Mendeleev's statements on the role of hydrates.

Klenkova's study of cellulose fibers showed that the hydrophilic properties, the amount of nonfreezing water contained in the fine capillaries of the fiber, and the pore content as determined by the sorption of various molecules characterize the state of the structure of the fibers, the density of packing, and to a certain extent the reactivity [10]. On comparison of the hydrophilic properties of cellulose fibers and chitin [11] it was found that the hygroscopic character of chitin exceeds that of ramie and is close to that of mercerized wood cellulose (Table 1),

TABLE 1. Hydrophilic Properties of Chitin and Cellulose Fibers

Material investigated	Regain (% on wt. of dry substance) at RH of		Amount of nonfreezing water at −6° after saturation at 100% RH (% on wt. of dry substance)
	65%	100%	
Chitin	8.9	34.7	1.4
Ramie fiber	5.5	19.7	12.5
Mercerized fibers (viscose wood cellulose)	8.96	32.6	26.2

TABLE 2. Internal Surface According to Data on the Adsorption of Nitrogen at Its Boiling Point (according to the experiments of Klenkova and Pyaivinen)

Material	Internal surface (sq.m/g)	
	original	P_{ptd} from H_3PO_4 solution
Chitin	2.1	99
Cotton cellulose	1.7	267

but the amount of nonfreezing water is considerably higher in ramie than in chitin. The moisture absorbed by chitin at 100% relative humidity freezes almost completely at −6°, which indicates that in chitin the active surface accessible to moisture is smaller than in cellulose. The moisture absorbed by chitin is probably in the coarse capillaries, where it readily freezes.

A study of the heats of swelling of chitin and cellulose in water indicates that the heat of wetting of chitin with water is almost the same as that of ramie and is less than that of mercerized cellulose [11]. On the other hand in sodium hydroxide solutions air-dry cellulose fibers swell considerably and the heat of swelling is higher than in water. For chitin the heat of swelling increases only slightly at alkali concentrations of 17.5% and 23%, but increases sharply at 34.5% of sodium hydroxide, which is probably associated with the powerful action of alkali on chitin at these concentrations. The values of the heats of swelling of cellulose and chitin in sodium hydroxide solutions indicate the low degree of interaction between chitin and alkali and the lower accessibility of the reaction centers in the structure of chitin than in the structure of cellulose.

A study of the internal surface of chitin by the method of the low-temperature adsorption of nitrogen showed that the original chitin has an internal surface approximately equal to that of cellulose, whereas the surface of chitin precipitated from its solution in phosphoric acid is 50 times as great as that of the original chitin and only one-third of the surface of cotton cellulose treated under similar conditions (Table 2).

The extremely low reactivity of the original chitin may be explained by the inaccessibility of its reaction centers to reagents. This is illustrated well by a comparison of the dissolutions of chitin and cotton wool in phosphoric acid. Whereas cotton wool is immediately impregnated with solvent and converted into a gel, the scales of chitin do not swell throughout its mass, but dissolved gradually in layers. The higher reactivity of regenerated cellulose as compared with regenerated chitin, which has been noted by many authors [12, 13], is in good accord with data on the greater internal surface of the cellulose fiber. The low reactivity of chitin is shown particularly in the difficulty in the preparation of its esters. In contrast to cellulose, chitin is difficult to nitrate and acetylate, though for cellulose these reactions have been carried out for years on the large scale.

It was found that the nitration mixtures that are generally used for cellulose are not suitable for chitin because sulfuric acid brings about the decomposition of chitin. Schorigin and Hait [14] obtained the best results with concentrated nitric acid (sp. gr. 1.50). The chitin nitrate obtained by these authors contained only 7.5% of nitrogen, did not dissolve in organic solvents, and was partially soluble in formic acid. These authors described also the

TABLE 3. Synthesis of Tosyl Esters of Chitin

| Expt. No. | No. of moles of reagent per mole of chitin | | Reaction time (days) | Sulfur content (%) | | Decomp. temp. (°C) |
	p-Toluene sulfonil chloride	pyridine		total	in soluble part	
1	2	40	9	0,3	—	—
2	5	45	10	5,73	8,62	145—150
3	8	45	10	6,89	—	150—160
4	10	45	5	7,58	9,26	155—160
5	10	67	10	6,71	8,47	155—160
6	10	40	7	7,52	—	—
7	10	54	10	10,22	—	154—156
8	15	45	5	7,52	—	152—153

TABLE 4. Synthesis of Mesyl Esters of Chitin

| Expt. No. | No. of moles of reagent per mole of chitin | | Reaction time (days) | Sulfur content (%) | Decomp. temp. (°C) |
	pyridine	Methane-sulfonyl chloride			
1	40		2	9,55	—
2	40	10	3	6,90	160 (carbonization)
3	40		7	12,57	170 (carbonization)
4	70		20	11,09	154—157 (decomposition)

acetylation of chitin [15]. They succeeded in effecting the almost complete acetylation of chitin by the passage of dry hydrogen chloride in acetic anhydride. Chitin acetate was then obtained as an amorphous mass that was difficult to filter off. Hence, the acetylation of chitin occurred not under homogeneous, but under typically heterogeneous conditions, for the product was obtained as a gel, which possibly held the reaction back.

We synthesized the tosyl and mesyl esters of chitin with the object of using them in further synthesis by means of replacement or cleavage with formation of anhydrides (Pyaivinen's experiments). Tosyl and mesyl esters have been described earlier for cellulose, and the reaction was carried out in a pyridine medium, but there is no reliable and generally accepted method of activation of cellulose for these reactions. For the activation of chitin for tosylation we used its reprecipitation from its 3% solution in 80% phosphoric acid, dissolution being for 17 hours at room temperature. For the removal of water and to bring about "inclusion" we used pyridine. Unlike the original chitin, the chitin activated in this way dissolved in formic acid. The phosphoric acid effected partial removal of the acetyl groups, which was indicated by van Slyke analysis for primary amino groups. The determination of the intrinsic viscosity of the regenerated chitin in 80% H_3PO_4 (24 hours' dissolution) showed that its intrinsic viscosity had been reduced by one-half.

Table 3 gives the results on the tosylation of chitin, from which it will be seen that with increase in the number of molecular proportions of p-toluenesulfonyl chloride there is a rise in the sulfur content of the reaction products. Comparison of Expts. 4 and 8 shows that further increase in the amount of p-toluenesulfonyl chloride (above 10 moles) no longer affects the degree of substitution. The same is observed for the tosyl esters of cellulose [13].

The experiments showed that the optimum proportions of chitin, tosyl chloride, and pyridine are 1 : 10 : 50. The degree of substitution depends essentially on the amount and concentration of p-toluenesulfonyl chloride and on the time. Too great an excess of pyridine lowers the degree of substitution. Monotosyl esters of chitin dissolve partially in pyridine and benzyl alcohol; at sulfur contents of less than 8% the samples carbonize, but more highly substituted products melt with decomposition at 155-160°. The ready hydrolyzability of the tosyl groups with 0.5 N NaOH (Murray's method) provides proof of the fact that these groups are substituted at hydroxy groups, and not at the nitrogen of C−2.

TABLE 5. Conditions of the Preparation of Ethylcellulose and Ethylchitin

Starting material	No. of moles		Ethylation conditions	OC_2H_5, %	Degree of substitution	Solubility
	C_2H_5Cl	NaOH				
Chitin	12	14	1 hr 60°	26,50	1,36	Ha 40—60% in alcohol-benzene
	15	16	1 hr 80°	26,43	1,36	
Cellulose	12	14	8 hr 130°	46,60	2,25	Completely in alcohol-benzene
	15	16		46,80	2,26	

TABLE 6. Preparation Conditions and Properties of CMCh

NaOH concn. (%)	No. of moles per mole of chitin		Reaction time (hr)	Temp. (°C)	Amt. of chitin taken (g)	Amt. of chitin that reacted (%)	Na (%)		Degree of substitution of sol. part	Viscosity of 1% soln (centipoise)	$[\eta]$ in 6% NaOH
	NaOH	Chloro-acetic acid					sol. part	swollen part			
49,2	6	3	20,0	20	7,0	93,0	7,93	2,52	0,97	22,18	3,20
				40	7,0	76,0	8,76	2,62	1,08	11,13	2,20
				60	7,0	60,0	7,21	3,76	0,88	26,06	3,20
49,7 *	6	3	18,5	40	3,4	88,2	7,25	3,91	0,88	22,84	1,90
			12,0	60	2,7	88,8	6,13	2,30	0,75	30,20	—

* The chitin was treated with excess of alkali.

As well as the tosyl esters of chitin, we prepared also its mesyl esters (Table 4). For this purpose, chitin precipitated from alkaline solution [16] was repeatedly washed with water and "included" by solvent displacement with pyridine. The chitin activated in this way was cooled to 4° and treated with a pyridine solution of methanesulfonyl chloride cooled to 4°. On mixture of the reactants, heat was evolved and the mixture became dark brown. The synthesis was carried out at room temperature. As will be seen from Table 4 (Expt. 3), the highest sulfur content was obtained on treatment of chitin with methanesulfonyl chloride for seven days. The monomesyl ester should contain 11,38% of sulfur. Mesyl esters of chitin swell in dilute solutions of acids and alkalis, and the sample from Expt. 4 swelled strongly in water.

For the synthesis of ethers, the activation of chitin, like that of cellulose, is usually carried out by a preliminary treatment of the starting materials with alkaline solutions. It is known [17] that the methylation of chitin with dimethyl sulfate proceeds more slowly than that of cellulose. Thus, after a 15 fold methylation we obtained a methyl ether of chitin containing 16% of OCH_3.

Ethylation under our conditions [18] proceeded more satisfactorily. By the ethylation of chitin in an autoclave with agitation we obtained ethylchitin containing 33.3% of ethoxy groups. Such ethylchitin is completely soluble in ketones, hydrocarbons, and mixtures of various solvents; it gives clear solutions of 5% concentration, from which films can be cast with reasonable mechanical properties [18]. Table 5 gives the results of comparable experiments on the ethylation of cellulose and chitin, which had been first treated with 40% NaOH, in sealed tubes.

It will be seen from Table 5 that the ethylation of cellulose proceeds more to completion than that of chitin. We have previously prepared glycerol [19] and hydroxyethyl [18] ethers of chitin. To carry out the synthesis of these ethers successfully it is essential to subject chitin to swelling in alkali with freezing and thawing or to vacuum impregnation at ordinary temperature. In the preparation of such ethers of cellulose one starts from alkali celluloses obtained in the usual way. We have recently carried out the synthesis of water-soluble carboxymethylchitin (CMCh) under conditions analogous to those for the synthesis of carboxymethylcellulose (CMCe)

$$[C_6H_7O_2(NHCOCH_3)(OH)_2] \xrightarrow[\text{NaOH}]{\text{ClCH}_2\text{COOH}} \longrightarrow [C_6H_7O_2(NHCOCH_3)(OH)_{2-x}(OCH_2COONa)_x]_n$$

CMCh, like CMCe, may find application in drilling fluids, as detergents and emulsifiers, and for other purposes.

Preliminary experiments on the synthesis of CMCh showed that, when alkali chitin obtained by the impregnation of chitin with 20-33% sodium hydroxide solution is used, water-soluble CMCh is not formed. Increase in the alkali concentration to 40-50% ensures the synthesis of CMCh that dissolves in water [20]. Alkali chitin was prepared in two ways: 1) treatment of chitin with excess of alkali for 24 hours at room temperature, followed by squeezing to three times the original weight; 2) treatment of chitin with the required amount of alkali at room temperature for three hours. When chitin is treated with excess of alkali solution with a subsequent squeeze, then on treatment with chloroacetic acid there is some rise in the amount of chitin that reacts, even at a higher temperature with a shorter reaction time. However, it is desirable to carry out the reaction with alkali chitin obtained by treatment with the calculated amount of alkali for three hours, because the consumption of alkali and the duration of the impregnation of the chitin are reduced, and at the same time there is the possibility of preparing CMCh at room temperature with maximum yield of the water-soluble part (up to 93%) without hydrolysis of the nitrogen-attached acetyl group (Table 6).

In our laboratory we have recently carried out work with object of finding methods of synthesizing cellulose ethers that are technologically and economically more rational. Our laboratory has endeavored to find alkyl carriers that will ensure synthesis in the direction of ethers and will make the process more economic. We tried thioethers, aliphatic diazo compounds, and benzenesulfonic esters. Thus, we carried out syntheses of cellulose ethers under strictly homogeneous conditions, e.g., in an organic base, and by the use of benzenesulfonic esters we succeeded in obtaining higher-alkyl ethers having peculiar and useful physicochemical and physicomechanical properties. As the number of carbons in the chain increased, the hydrophobic character increased, the softening temperature fell, and the mechanical properties were characterized by higher plasticity [21].

TABLE 7. Alkylation of Cellulose in Benzyltriethylammonium Hydroxide Solution

Alkylation reagent	No. of moles of ester per mole of cellulose	Temp. (°C)	Time (hr)	Degree of substitution	$[\eta]$	Viscosity of 1% soln. (centipoise)	Solubility
$C_6H_5SO_2$—OCH_3	5,0	55	0,5	1,38	—	—	In water
	7,0	55	4,0	1,60	—	—	In dil. alkali
$C_6H_5SO_2$—$OCH(CH_3)_2$	6,0	40	2,0	0,22	2,85	13,6	In 1% NaOH
	6,0	50	2,0	0,22	2,45	4,7	
$C_6H_5SO_2$—$OC(CH_3)_3$	8,0	50	2,0	0,34	6,30	205,0	In water
$C_6H_5SO_2$—$OCH_2CH=CH_2$	6,0	70	2,0	0,25	5,70	171,0	
	3	50	2,0	0,32	3,6	—	In 2% NaOH

On alkylation of cellulose in an organic-base solution of methyl, isopropyl, t-butyl, or allyl benzenesulfonate, the corresponding cellulose ether is formed at a low degree of substitution; such ethers are soluble in 1-2% NaOH or in water, as will be seen from Plisko's experiments (Table 7). Special interest is presented by the t-butylcelluloses of degree of substitution 0.25-0.34, because they dissolve in water with formation of viscous solutions having adhesive properties. Alkali-soluble methylcelluloses are obtained also by the alkylation of cellulose in a solution of the sodium iron tartrate complex. We have not yet succeeded in preparing the analogous ethers of chitin, because the latter is not soluble in the above-indicated solvents.

SUMMARY

On comparison of the reactivities of chitin and cellulose in their conversion into ethers and esters it is found that chitin is considerably less reactive than cellulose, which is to be attributed to a difference in the internal active surfaces.

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CATALYTIC PROPERTIES OF RARE-EARTH ELEMENTS

COMMUNICATION 1. TRANSFORMATIONS OF HEPTANE, CYCLOHEXANE, AND ETHYLCYCLOPENTANE OVER ERBIUM OXIDE

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Scarcely any investigation has been made of the catalytic properties of rare-earth elements in the transformations of hydrocarbons. There are only a few papers [1-3], in which the use is reported of cerium, samarium, and neodymium oxides and of mixed catalysts consisting of $Ce_2O_3 \cdot Al_2O_3$ and $Nd_2O_3 \cdot Al_2O_3$. To various extents all these catalysts brought about the dehydrogenation of cyclohexane and the dehydrocyclization of heptane. In the investigation [4] the activation energy was determined for the dehydrogenation of cyclohexane over cerium oxide; it was found to be 32 kcal/mole.

In the present investigation we studied the catalytic properties of erbium oxide and of a mixed catalyst containing 15% of erbium oxide and 85% of alumina in the transformations of cyclohexane, heptane, and ethylcyclopentane at 545-590° in a flow system at atmospheric pressure in a stream of hydrogen. Under the given conditions both these catalysts bring about the partial dehydrogenation of cyclohexane to benzene and the dehydrocyclization of heptane to toluene. From ethylcyclopentane toluene was obtained only over the mixed catalyst. Under the experimental conditions heptane and ethylcyclopentane underwent considerable hydrocracking over both catalysts.

EXPERIMENTAL

Catalysts. Commercial erbium oxide of 99% purity was dissolved in dilute nitric acid. The hydroxide was precipitated from the solution of the nitrate with dilute ammonia, filtered off, washed free from NO_3^- ions, dried at 120°, tableted into 4 · 4 mm cylinders, and roasted at 500° for six hours. The catalyst Er_2O_3/Al_2O_3 was prepared by the mixing of 15 parts by weight of Er_2O_3 and 85 parts by weight of Al_2O_3. The specific surfaces of the catalysts prepared in this way were determined by the dynamic method [5] and were found to be 22.3 sq.m/g for Er_2O_3 and 190 sq.m/g for Er_2O_3/Al_2O_3.

Hydrocarbons. Ethylcyclopentane was synthesized by the Grignard reaction of cyclopentanone with ethylmagnesium bromide, followed by the dehydration of 1-ethylcyclopentanol by means of iodine and the hydrogenation of 1-ethyl-1-cyclopentene in presence of 20% of nickel on alumina. The resulting ethylcyclopentane, and also cyclohexane and heptane, was fractionated through a column of 50 plate efficiency. When analyzed chromatographically the original hydrocarbons gave no peaks attributable to other hydrocarbons. The properties of the original hydrocarbons and the constants given in the literature are presented in Table 1.

Experimental procedure and analysis of catalysis products. The experiments were carried out in a flow apparatus at 545-590° in a stream of hydrogen at atmospheric pressure. In all experiments the space velocity of the feed of the substances investigated was 0.25 hr^{-1}. A quartz reactor was charged with 10 ml of catalyst (12.94 g of Er_2O_3 and 6.90 g of Er_2O_3/Al_2O_3). Before each experiment the catalyst was activated with hydrogen at 550° for six hours. After each experiment the catalyst was regenerated with air diluted with nitrogen to an oxygen content of 5-7% at 500-520°. In the process of regeneration a determination was made of the amount of coke deposited on the catalyst. With this object the outgoing gases were passed through two successive ascarite tubes, in which carbon dioxide was completely absorbed. The experiments were usually of 4-5 hours' duration. Catalyzate was taken after every two hours, and the first portion was somewhat smaller than subsequent ones because of the higher cracking activity of the catalyst in the intial period of its work and the losses in priming the system.

The liquid catalyzates were analyzed on a gas-liquid chromatograph [8]. The iodine values of the catalyzates were determined by Kaufmann's method [9]. The gaseous catalysis products were analyzed on an adsorption chro-

TABLE 1. Properties of Original Hydrocarbons

Hydrocarbons	Our results			Data in literature			Literature ref.
	b.p. (°C at 760 mm)	n_D^{20}	d_4^{20}	b.p. (°C at 760 mm)	n_D^{20}	d_4^{20}	
Heptane	98,2	1,3875	0,6837	98,4	1,3876	0,6837	[6]
Cyclohexane	80,4	1,4258	0,7779	80,7	1,4262	0,7785	[6]
Ethylcyclopentane	103,7	1,4198	0,7661	103,5	1,4198	0,7665	[7]

TABLE 2. Yields of Liquid Catalyzate, Gas, and Coke (% on original hydrocarbon)

Hydrocarbon	Catalyst	Temp. (°C)	Liquid catalyzate	Gas	Coke
C_6H_{12}	Er_2O_3/Al_2O_3	545	80,4	14,5	0,5
C_6H_{12}	Er_2O_3/Al_2O_3	560	79,3	16,8	1,0
C_6H_{12}	Er_2O_3/Al_2O_3	590	59,5	38,1	1,8
C_6H_{12}	Er_2O_3	545	88,0	8,5	0,6
C_6H_{12}	Er_2O_3	560	84,4	12,3	1,3
C_6H_{12}	Er_2O_3	590	78,1	15,9	2,0
C_7H_{16}	Er_2O_3/Al_2O_3	545	45,7	50,2	1,0
C_7H_{16}	Er_2O_3/Al_2O_3	560	32,2	61,2	1,2
C_7H_{16}	Er_2O_3	545	57,6	35,4	1,1
C_7H_{16}	Er_2O_3	560	42,4	51,8	1,4
C_7H_{14}	Er_2O_3/Al_2O_3	545	51,1	45,4	3,0
C_7H_{14}	Er_2O_3	545	72,1	20,9	1,9
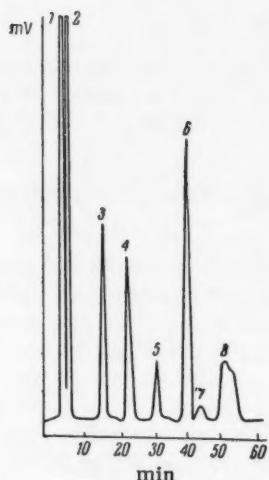
Fig. 1. Chromatogram of gas obtained in the passage of cyclohexane over Er_2O_3/Al_2O_3 at 590°: 1) Hydrogen; 2) methane; 3) ethane; 4) ethylene; 5) propane; 6) propene; 7) butane-isobutane; 8) butenes.
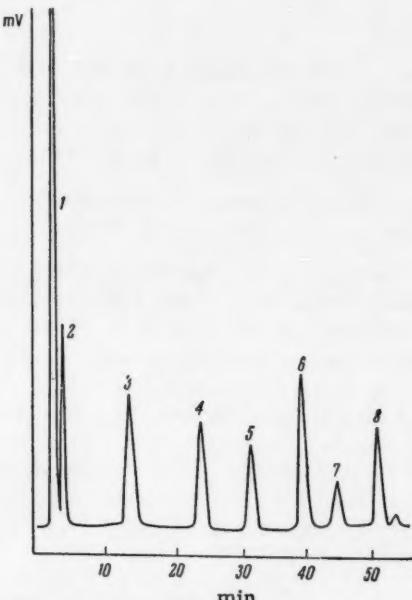

Fig. 2. Chromatogram of gas obtained in the passage of heptane over Er_2O_3 at 545°: 1) Hydrogen; 2) methane; 3) ethane; 4) ethylene; 5) propane; 6) propene; 7) butane-isobutane; 8) butenes.

TABLE 3. Composition of Gas (%) from Data of Chromatographic Analysis

Catylyst	Temp., C°	Hydro—carbon	H_2	CH_4	C_2H_6	C_2H_4	C_3H_8	C_3H_6	C_4H_{10}	C_4H_8
Er_2O_3/Al_2O_3	545	C_7H_{16}	47,9	6,0	8,0	9,4	6,1	10,7	7,9	4,0
Er_2O_3	545	C_7H_{16}	79,6	4,2	3,6	5,8	1,4	3,3	0,4	1,7
Er_2O_3/Al_2O_3	560	C_6H_{12}	83,5	4,0	2,1	4,0	0,8	4,0	1,0	0,6
Er_2O_3	560	C_6H_{12}	88,4	3,7	1,6	2,2	0,6	3,4	0,1	—
Er_2O_3/Al_2O_3	590	C_6H_{12}	71,9	7,5	3,7	4,0	0,7	3,9	1,7	4,3
Er_2O_3/Al_2O_3	545	C_7H_{14}	70,0	5,5	3,5	6,4	0,9	8,9	0,5	4,3
Er_2O_3	545	C_7H_{14}	84,3	6,3	3,3	2,8	0,1	1,9	0,1	1,2

TABLE 4. Compositions of Liquid Catalyzates (%) from Data of Chromatographic Analysis

Catalyst	Temp. (°C)	Cyclohexane				Heptane		
		Composition of catalyzate						
		benzene	methyl-cyclo-pentane	cyclo-hexene	cyclo-hexane	toluene	benzene	heptane
Er_2O_3/Al_2O_3	545	4,1	0,7	—	95,2	4,8	1,1	94,1
Er_2O_3/Al_2O_3	560	6,9	1,6	0,7	90,7	10,9	1,2	87,9
Er_2O_3/Al_2O_3	590	28,6	3,6	2,1	65,7			
Er_2O_3	545	1,7	1,4	—	96,9	5,0	1,1	93,9
Er_2O_3	560	8,6	1,6	1,4	88,4	11,6	1,9	86,5
Er_2O_3	590	13,1	0,8	2,5	83,5			

matograph with a thermal-conductivity detector. The adsorbent filling the column was alumina of particle size 0.25-0.5 mm. The column was 6 mm in diameter and 220 cm in length. The volume of the sample analyzed was 2.5 ml. During the analysis the temperature of the column was changed from that of the room to 190° in the course of 30 minutes. Detection was carried out by the hydrogen method [10].

The experimental results obtained in the catalytic treatments of cyclohexane, heptane, and ethylcyclopentane are presented in Tables 2, 3, and 4.

As will be seen from Table 2, in the transformation of cyclohexane over the mixed catalyst with rise in temperature from 545 to 590° the yield of liquid catalyzate falls from 80% to 59% and simultaneously the yields of gaseous products and coke rise from 14.5% to 38.1% and from 0.5% to 1.2% respectively. In the transformation of the same hydrocarbons over pure erbium oxide the yield of liquid catalyzate was 88% at 545° and 78.1% at 590°, and the yield of gaseous products changed from 8.5% (545°) to 15.9% (590°). The amount of coke deposited on this catalyst was about the same as in the case of the mixed catalyst. It follows from Table 2 that also in the transformations of the other two hydrocarbons the yields of liquid catalyzates were considerably higher over pure erbium oxide than over the mixed catalyst. However, these yields, obtained in the transformations of heptane and ethylcyclopentane, were considerably less than in the case of cyclohexane, which is to be explained, of course, by the lower stabilities of these hydrocarbons. Hence, as compared with the mixed catalyst, pure erbium oxide has much less cracking power.

Table 3 gives the results of the analysis of the gaseous catalysis products.

As will be seen from Table 3, in all cases the gas obtained over the mixed catalyst is richer in hydrocarbons than the gas obtained over Er_2O_3. In the transformations of cyclohexane and heptane over erbium oxide the amounts of saturated and unsaturated hydrocarbons are approximately the same. In the catalytic treatment of ethylcyclopentane over the mixed catalyst the resulting gas contained 19.6% of unsaturated and 10.4% of saturated hydrocarbons. In Figs. 1 and 2 we give examples of the gas-analysis chromatograms. Table 4 gives the results of the analysis of liquid catalyzates by gas-liquid chromatography.

Before we examine Table 4 it must be mentioned that in the analysis of liquid catalyzates peaks were observed on some chromatograms that belonged to hydrocarbons of lower molecular weight than those given in Table 4. However, the amount of these hydrocarbons did not exceed 1-2%. As will be seen from Table 4, the catalyzate obtained in the transformation of cyclohexane consisted of unchanged hydrocarbon, benzene, methylcyclopentane, and cyclohexene. The benzene content of the catalyzate obtained over the mixed catalyst at 545° was 4.1%, and at 590° it attained 28.6%. Over pure erbium oxide at these temperatures we obtained 1.7% and 13.1% of benzene, respectively. The chromatogram of the catalyzate obtained from cyclohexane over the mixed catalyst at 590° is presented in Fig. 3.
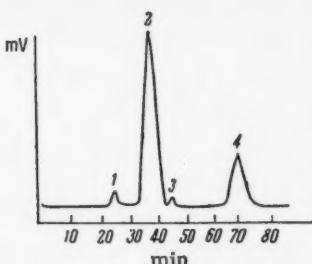
Fig. 3. Chromatogram of the catalyzate obtained in the passage of cyclohexane over Er_2O_3/Al_2O_3 at 590°: 1) Methylcyclopentane; 2) cyclohexane; 3) cyclohexene; 4) benzene (70°); velocity of gas carrier 60 ml/min.

In the transformation of heptane, unchanged heptane, toluene and benzene were identified in the catalyzate. Table 4 shows that the contents of aromatic hydrocarbons in the liquid catalyzates were almost the same for the mixed catalyst and for pure erbium oxide. However, the yields of liquid catalyzate were appreciably larger over pure erbium oxide than over the mixed catalyst (see Table 2). Thus, over Er_2O_3 we obtained more aromatic hydrocarbons (calculated on the original hydrocarbon) than over the mixed catalyst. The presence of benzene in heptane catalyzates indicates the occurrence of demethylation. Chromatographic analysis of the catalyzate obtained in the passage of ethylcyclopentane over pure erbium oxide did not reveal toluene, whereas 8.3% of toluene was found in the catalyzate obtained over the mixed catalyst.

The iodine values of catalyzates obtained in the transformations of cyclohexane and heptane over both catalysts did not generally exceed 15, except in the case of the cyclohexane catalyzate obtained at 590° over Er_2O_3/Al_2O_3, for which the iodine value was 29. For the ethylcyclopentane catalyzates the iodine values were 29 and 52, respectively, for Er_2O_3 and Er_2O_3/Al_2O_3.

SUMMARY

1. An investigation was made of the catalytic properties of erbium oxide and erbium oxide on alumina in the transformations of cyclohexane, ethylcyclopentane, and heptane at 545-590° in a flow system.

2. Under the given conditions these catalysts bring about the dehydrogenation of cyclohexane to benzene, the dehydroisomerization of ethylcyclopentane to toluene, and the dehydrocyclization of heptane to toluene.

3. Under the given conditions in presence of these catalysts the original hydrocarbons undergo cracking reactions, the extent of which depends on the temperature of the experiment and the structure of the hydrocarbon.

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BRIEF COMMUNICATIONS

SYNTHESIS OF 2-METHYLACETOACETIC ESTER

BY THE METHYLATION OF ACETOACETIC ESTER

WITH DIMETHYL SULFATE

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In 1937 Knunyants proposed a method of synthesizing 2-methylacetoacetic ester by the methylation of aceto-acetic ester with dimethyl sulfate in presence of aqueous alkali [1]. We have repeated this synthesis and investigated the composition of the reaction products by chromatography on plates of unbound alumina. Though the author refers to a yield of 97-98% in this method, it follows from the chromatographic results that in actuality a mixture of products is formed and this consists of about 60% of 2-methylacetoacetic ester and 40% of unchanged acetoacetic ester. 2,2-Dimethylacetoacetic ester is formed in only a very small amount (2-3%).

$$CH_3COCH_2COOC_2H_5 \xrightarrow[-H_2O]{+HN(CH_3)_2} CH_3-C=CH-CO_2C_2H_5 \xrightarrow[90-100°]{(CH_3)_2SO_4}$$
$$:N(CH_3)_2 \quad (I)$$

$$\longrightarrow CH_3-\underset{\overset{||}{+N(CH_3)_2}\,[CH_3SO_4]^-}{\overset{CH_3}{C}}-CH-CO_2C_2H_5 \xrightarrow[20-30°]{H_2O} CH_3COCHCOOC_2H_5 + H_2\overset{+}{N}(CH_3)_2[CH_3SO_4]^-$$
$$(II)$$
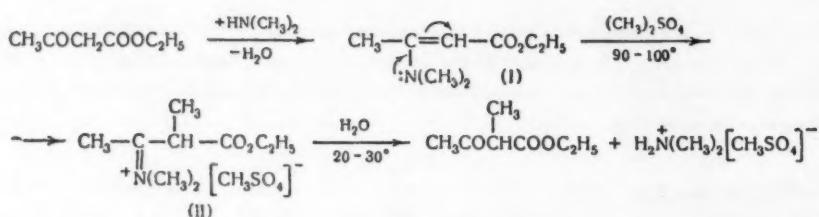
In the present paper we propose a convenient preparative method for the synthesis of pure 2-methylaceto-acetic ester, free from contamination with dimethylacetoacetic ester and with the original acetoacetic ester. The synthesis is based on the methylation of readily accessible derivative of acetoacetic ester, namely 3-dimethylamino-crotonic ester (I), with dimethyl sulfate at an elevated temperature (cf. [2]). The methylation of (I) goes quantita-tively with transfer of the reaction center, and after the hydrolysis of the quaternary salt (II) 2-methylacetoacetic ester is formed in 80% yield.

EXPERIMENTAL

Chromatography was carried out on horizontal plates (13 · 18 cm) with alkaline Al_2O_3 of activity 5; the thickness of the adsorbent layer was 0.4-0.5 mm. Benzene was used for the elution of the chromatograms, and iodine vapor was used to develop the spots. A quantitative estimate was carried out by means of parallel experiments with mixtures of known composition.

Methylation of acetoacetic ester with dimethyl sulfate in presence of aqueous alkali. This was carried out by the described method [1], and the reaction product was analyzed chromatographically. We obtained two spots of about equal intensity having R_f 0.24 and 0.55 (a sample of dimethylacetoacetic ester gave a spot having R_f 0.66).

3-Dimethylaminocrotonic ester (I). This was prepared by passing gaseous dimethylamine into acetoacetic ester [3] or from acetoacetic ester and a 30% aqueous solution of dimethylamine: we added 400 ml of 30% aqueous dimethylamine with stirring and cooling to 260 ml (2 moles) of acetoacetic ester. The temperature of the mixture was kept below 10°. Stirring was continued for one hour, and with cooling (below 10°) 200 g of anhydrous potassium carbonate was added, after which stirring was continued for 40 minutes. Benzene (200 ml) was added, and the organic layer was separated and vacuum-distilled. We obtained 200 g (63%) of 3-dimethylaminocrotonic ester (I), b.p. 115-118° (7-8 mm).

2-Methylacetoacetic ester. To 199 g (1.27 moles) of 3-dimethylaminocrotonic ester heated to 95° gradual addition was made of 132 ml (1.4 moles) of dimethyl sulfate at such a rate that the temperature of the mixture did not exceed 100° (90-100°, on cooling below 90° the reaction is arrested). After the whole of the dimethyl sulfate had been added (about 45 minutes), the mixture was heated at 95° for 45 minutes, cooled to 35°, and stirred (about 5 minutes) with 200 ml of ether. The ether was decanted as completely as possible from the thick oil, to which water (250 ml) was then added; the resulting mixture was poured into a separating funnel. After 20-40 minutes (depending on the temperature) hydrolysis was complete, and the layer of methylacetoacetic ester was separated; the aqueous layer was extracted with ether, and the ether extract was combined with the main part of the product; drying and distillation followed. We obtained 147.4 g (80.5%) of 2-methylacetoacetic ester, b.p. 92-93° (33 mm); in chromatography on Al_2O_3 it gave one spot having $R_f = 0.55$.

SUMMARY

1. On methylation of acetoacetic ester with dimethyl sulfate a mixture is formed of approximately equal amounts of 2-methylacetoacetic ester and acetoacetic ester.

2. Pure 2-methylacetoacetic ester was prepared by the methylation of 3-dimethylaminocrotonic ester with dimethyl sulfate.

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2-BROMOHEXAFLUOROISOBUTYRIC ACID

AND ITS DERIVATIVES

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Extensive studies of the chemical properties of perfluoroisobutene led to the synthesis of numerous compounds of the perfluoroisobutyric acid series in which α-fluorine is replaced by hydrogen [1], nitro [2], and hydroxyl [3]. We now describe the synthesis of 2-bromohexafluoroisobutyric [2-bromo-3,3,3-trifluoro-2-(trifluoromethyl)propionic] acid and its derivatives. For this purpose we made use of 1,2-dibromo-1,3,3,3-tetrafluoro-2-(trifluoromethyl)propyl ethyl ether (I), which is formed by the action of bromine on ethyl perfluoroisobutenye [1,3,3,3-tetrafluoro-2-(trifluoromethyl)propenyl] ether [4].

On treatment of (I) with concentrated sulfuric acid, elimination of ethyl bromide occurs with formation of 2-bromohexafluoroisobutyryl fluoride (II):
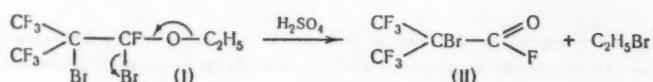
The sulfuric acid facilitates the displacement of a pair of electrons from alkyl to oxygen. The thermal decomposition of $CH_3OCFBrCFClBr$ proceeds by an analogous scheme [5]. (II) was converted into 2-bromohexafluoroisobutyric acid and its derivatives (the amide, anilide, and methyl and ethyl esters).

EXPERIMENTAL

2-Bromohexafluoroisobutyryl fluoride. Ethyl perfluoroisobutenyl ether (43.5 g) was added gradually to 11.6 ml of dry bromine at 20°. Unchanged bromine was removed by washing with 20% KOH solution. The crude bromo compound was placed in a distilling flask together with 20 ml of concentrated sulfuric acid. The mixture was heated until distillation began. The distillation was carried out in such a way that the temperature in the vapor did not exceed 50-55°. The further fractionation of the distillate gave:

1. Ethyl bromide, 19.6 g, b.p. 36-38°. This was identified in the form of the diethyl ether of hydroquinone; m.p. alone and in admixture with a known sample 70-71°.

2. 2-Bromohexafluoroisobutyryl fluoride, 25.6 g (48% on the ethyl perfluoroisobutenyl ether taken); b. p. 54.5-55°; n_D^{20} 1.3170. On being distilled it solidified in the condenser. Found: C 17.19; F 47.01%. C_4F_7OBr. Calculated: C 17.35; F 48.02%.

2-Bromohexafluoroisobutyric acid. This was prepared by hydrolysis of the acid fluoride, m.p. 117-121°, hygroscopic. Mol. wt. found by titration 277; calculated value 275.

2-Bromohexafluoroisobutyramide. This was prepared by the reaction of a solution of 2.7 g of the acid fluoride in 10 ml of ether with 2.5 ml of 15% aqueous ammonia. Yield 1.4 g (54%); m.p. 126-127° (from heptane). Found: C 17.58; H 0.91; F 42.20; N 4.97%. $C_4H_2F_6BrON$. Calculated: C 17.53; H 0.74; F 41.61; N 5.11%.

2-Bromohexafluoroisobutyranilide. The experiment was carried out as described for the acid fluoride, the reactants being 22 g of ethyl perfluoroisobutenyl ether, 7 ml of bromine, and 11 ml of concentrated sulfuric acid, and the distillate was collected in a solution of 23 g of aniline in 25 ml of dry ether. The mixture was treated with dilute hydrochloric acid, the ether layer was separated, and ether was evaporated off. We obtained 21.3 g (62.5% on the amount of ethyl perfluoroisobutenyl ether taken) of 2-bromohexafluoroisobutyranilide, m.p. 95-96° (from benzene). Found: C 34.45; H 1.70; F 32.38; N 4.02%. $C_{10}H_6F_6BrON$. Calculated: C 34.30; H 1.73; F 32.56; N 4.00%.

Methyl 2-bromohexafluoroisobutyrate. This was prepared similarly from 80 g of ethyl perfluoroisobutenyl ether, 20 ml of bromine, and 40 ml of concentrated sulfuric acid. The distillate was collected in 40 ml of dry methanol. The mixture was decomposed with water, and the organic layer was separated, dried with calcium chloride, and distilled. We obtained 57.4 g (56%) of methyl 2-bromohexafluoroisobutyrate, b.p. 115-120°. Redistillation gave a substance having: b.p. 119.5-120°; n_D^{20} 1.3556; d_4^{20} 1.8041. Found: C 20.81; H 1.04; F 39.77; Br 26.72%; MR 34.97. $C_5H_3F_6BrO_2$. Calculated: C 20.78; H 1.05; F 39.48; Br 27.65%; MR 35.55.

Ethyl 2-bromohexafluoroisobutyrate. This was prepared similarly from 64 g of ethyl perfluoroisobutenyl ether, 32 ml of bromine, 32 ml of concentrated sulfuric acid, and 40 ml of ethanol. Yield 49.3 g (58.6%); b.p. 126-132° Redistillation gave a substance having: b.p. 63-65° (65 mm); n_D^{20} 1.3578; d_4^{20} 1.6770. Found: C 23.84; H 1.66; F 37.63; Br 26.38%; MR 39.69. $C_6H_5F_6BrO_2$. Calculated: C 23.78; H 1.66; F 37.62; Br 26.37%; MR 40.16.

SUMMARY

2-Bromohexafluoroisobutyric acid and its derivatives were prepared.

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DENSITY OF N-METHYLFORMAMIDE

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N-Methylformamide is a good solvent for many inorganic salts and has interesting properties as a solvent; its dielectric constant is 182.4 at 25° [1]. In order to characterize the stability of the structure of pure N-methyl-formamide to temperature, which is necessary for the study of the properties of ionic solutions, we measured the density of this solvent in the range 0-50°. A carefully purified sample had m.p. about −3.5° and specific conductivity about $5 \cdot 10^{-6} \Omega^{-1} cm^{-1}$. The literature [1, 2] gives from $5 \cdot 10^{-5}$ to $2 \cdot 10^{-6} \Omega^{-1} cm^{-1}$ [1, 2].

EXPERIMENTAL

The measurements were carried out by the usual pycnometric method. The pycnometer was a dilatometer with a calibrated capillary and a ground stopper; its volume was 5 ml. The carefully washed pycnometer was rinsed out with alcohol, dried, cooled in air, and kept until it had constant weight. Filling it with distilled water during calibration and with solvent during the measurements was carried out with the aid of a capillary pipet. After being filled with water, the pycnometer was heated to 100° for 20 minutes to remove dissolved gases. Thermostating was carried out in a glass cylinder through which liquid from an ultrathermostat was circulated; the temperature was kept constant within ± 0.03°. The calibration was carried out at 0, 10, 15, 20, 25, 30, 40, and 50° with four positions of the water meniscus in the capillary for each temperature. The pycnometer was kept in the thermostat until the meniscus ceased to move in the capillary. After the measurement the pycnometer was wiped on the outside with alcohol, brought to room temperature, and weighed. All weighings were carried out on an analytical balance. The calibration figures fitted well to straight lines in the coordinates of pycnometer volume and reading of the scale of the capillary. N-Methylformamide was kept in an ampoule, in which it was sealed in a vacuum immediately after distillation through a column, and it therefore did not contain dissolved gases. The first measurement was made at 50°; the temperature was then lowered, and measurements were made at the required temperatures with the same sample of the solvent, which made it possible to avoid long contact between the solvent and air. Plotting of the results on a graph showed that over the range of temperatures investigated the density of N-methylformamide varies linearly with temperature. Determination of the coefficients by the method of least squares led to the equation:

$$\rho = 1.0203 - 0.0008674t \pm 0.0002 \tag{1}$$

Whence, at 25° we obtained $\rho = 0.9986$, and at 0° $\rho = 1.0203$. Data in the literature given by various authors apply to different temperatures and vary considerably among themselves. Thus, at 25° we have 0.9961 [3], 0.9976 [1], and 0.9988 [2]; judging from the electric conductivity it was in [2] that the purest sample, the closest to ours, was obtained. At 0° 1.0114 was obtained [3], which, like the value at 25°, differed greatly from ours. In view of the considerable complications in the purification of this solvent, such a scatter of results must be attributed to the presence of impurities. In our sample these were present in negligibly small amount, which can be seen from the electric conductivity of our solvent.

From equation (1) the coefficient of thermal expansion is $(1/V)(\partial V / \partial T) = (= 1/\rho)(\partial \rho / \partial T) = 0.000869 \, deg^{-1}$ at 25°. The temperature coefficient of the dielectric constant, found from the results of [1], is −0.0089 deg^{-1}. Hence, of the strongly associated liquids of high dielectric constant, N-methylformamide has the most unstable structure [4].

The fact that for this solvent there is a linear relation between density and temperature is of interest for its own sake.

SUMMARY

The density of N-methylformamide was measured over the range 0-50°.

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MECHANISM OF THE THERMAL DECOMPOSITION
OF CARBOXYLIC SALTS

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Recently, on the basis of indirect experimental data, Nenitzescu and co-workers [1] expressed the opinion that the long-known [2] thermal decomposition of silver trichloroacetate into trichloroacetic anhydride begins with the decomposition of this salt to dichlorocarbene

$$Cl_3C \cdot CO_2Ag \longrightarrow Cl_2C + CO_2 + AgCl,$$

and then proceeds by the following complex scheme:

$$Cl_2C + Cl_3C \cdot CO_2^- Ag^+ \longrightarrow [Cl_3C \cdot CO \cdot O \cdot CCl_2]^- Ag^+ \longrightarrow$$

$$\longrightarrow Cl_3C \cdot COCl + CO + AgCl$$

$$Cl_3C \cdot COCl + Cl_3C \cdot CO_2Ag \longrightarrow Cl_3C \cdot CO \cdot O \cdot OC \cdot CCl_3 + AgCl$$
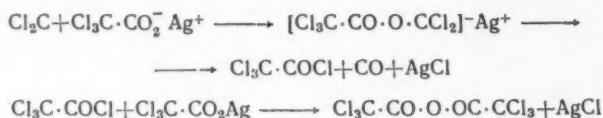
However, the present author and his coworkers [3] have shown for the case of a considerable number of silver, copper, and calcium salts of various carboxylic acids that, irrespective of the natures of the metal and the acid group, the first stage in the thermal decomposition of the salts is the elimination of the metal oxide and the formation of the acid anhydride, whereas the further transformations may proceed in the most diverse directions, depending on the properties of these primary reaction products.

As in the cases which we have studied of the thermal decomposition of salts the possibility of the primary formation of carbenes is practically excluded, Nenitzescu's suggestion about the mechanism of the conversion of silver trichloroacetate into trichloroacetic anhydride ceases to have a serious basis. It is evident that the formation in this case of small amounts of dichlorocarbene is either the result of secondary transformations of trichloroacetic anhydride under the influence of silver oxide (silver trichloroacetate, silver chloride) or is due to an independent side transformation of the original salt proceeding parallel to the main pyrolysis reaction. However, the formation of cyclopentene-1-carboxaldehyde, described by Nenitzescu for the reaction in cyclohexene, is due to the oxidative effect of the intermediately formed silver oxide, which has been noted several times before in other cases [3]. As regards Nenitzescu's statement that the simultaneous elimination of CO_2 and CO speaks in favor of his scheme, it should be noted that these two compounds have been frequently detected in the pyrolysis of various carboxylic salts [4] whose decomposition could not be associated with the primary formation of carbenes.

SUMMARY

The mechanism of the thermal decomposition of silver trichloroacetate is discussed.

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EFFECT OF SPINEL FORMATION ON THE REGENERABILITY

OF AN Ni — Al$_2$O$_3$ CATALYST

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It is known that nickelous oxide and alumina readily form the spinel NiAl$_2$O$_4$. Hedvall [1] obtained nickel aluminate from these oxides at 900° in four hours. Yander and Grob [2] obtained a spinel from NiO and α-Al$_2$O$_3$ at 1000-1100°, but Iida and Shimada [3] showed that the formation of a spinel from these oxides is appreciable already at 600°. Yamaguchi [4] showed that in the series MnO, ZnO, MgO, and NiO the ability to undergo spinel formation with alumina increases. The conditions for spinel formation are particularly favorable when the alumina is in the γ-phase, which has a defect spinel structure, i.e., a structure with vacant cation lattice points, or when precipitated nickel and aluminum hydroxides are roasted together [5, 6]. Thus, it is shown in [6] that a nonoriented spinel structure is already formed at 300° on roasting the precipitated hydroxides together. In the present paper we describe a case when spinel formation in the process of the regeneration of an Ni—Al$_2$O$_3$ catalyst leads to the loss of its activity.

EXPERIMENTAL

A catalyst of composition 10% by weight of Ni and 90% by weight of Al$_2$O$_3$ was prepared by the impregnation of commerical γ-Al$_2$O$_3$ with Ni(NO$_3$)$_2$ solution and reduction in a current of hydrogen with gradual rise in temperature from 120° to 360° over a period of 15-18 hours. Over this catalyst we carried out the hydrogenolysis of toluene to benzene with gradual raising of the temperature (to keep the conversion at a constant level) from 430° to 510° under a hydrogen pressure of 5 atm [7]. When, at 510°, the activity of the catalyst became low, the catalyst was regenerated by roasting it in a current of air at 500° for 5-6 hours and then reducing it under the conditions under which the original catalyst was prepared. This regeneration did not result in the recovery of the original activity. To study the reasons for the nonregenerability of the catalyst we carried out x-ray-diffraction photography (an RKL camera and a tube with an iron anode were used), determinations of magnetic susceptibility by the method described in [8], and determinations of texture from benzene vapor adsorption isotherms obtained by the dynamic method [9]. The results of these determinations for four samples of catalyst taken at different stages of its working cycle are given in the table.

As will be seen from the table, the phase compositions of the active (1) and inactive (2 and 4) samples were the same, i.e., one and the same crystalline phase of nickel (the cubic modification β-Ni) was active in the one case and inactive in the other. After oxidative roasting at 500°, which is used in the regeneration, the catalyst contains two crystalline phases, NiO and γ-Al$_2$O$_3$, which, as stated above, readily form a spinel.

The magnetic susceptibilities indicate that, in the first place, in the course of the working cycle the dimensions of the nickel crystals increase, because the susceptibility increases, and, in the second place, in the roasting of the catalyst in air the nickel is fully oxidized, because the susceptibility falls to 5.5. However, the reduction in dispersity, which causes a rise in magnetic susceptibility from 440 to 930, is not responsible for the loss in activity, because we specially kept one of the original samples at 430-480° in hydrogen until its susceptibility attained a value of 2200, and this sample was still active. Moreover, on the x-ray photographs we did not observe any change in the width of the nickel line at different stages of the working cycle, which indicates absence of considerable change in its dispersity. The specific surface, the mean pore radius, and the total pore volume of the catalyst varied in the range 15-20% in the course of the working cycle, i.e., no sharp changes which might lead to a great fall in activity in the course of the working cycle occurred.

Phase Composition, Magnetic Susceptibility, and Texture of an $Ni - Al_2O_3$ Catalyst at Different Stages of Its Working Cycle

Sample No.	Stage of work of catalyst	Catalytic activity	Crystalline phases found	Magnetic susceptibility $\lambda \cdot 10^6$ (CGSE units)	Specific surface S (sq. m/g)	Mean pore radius r (A)	Total pore vol. V (cc/g)
1	Before work	Active	β-Ni; γ-Al_2O_3	440	190	27	0,34
2	After 120 hours' work	Inactive	β-Ni; γ-Al_2O_3	810	164	32	0,33
3	After oxidative stage of regeneration	—	NiO; γ-Al_2O_3	5,5	189	—	—
4	After regeneration	Inactive	β-Ni; γ-Al_2O_3	930	160	35	0,35

The most probable cause of the deactivation of the catalyst must be sought in spinel formation from NiO and γ-Al_2O_3 in the oxidative roasting at 500°. It is known [10] that nickel that enters into the composition of the spinel $NiAl_2O_4$ is reduced with great difficulty and, under the conditions used in the reductive stage of the regeneration, is scarcely reduced at all. Hence, if part of the nickel goes in the formation of the spinel in the oxidation, then after regeneration the concentration of metallic nickel will be less than in the original catalyst. The relation of the catalytic activity of Ni−Al_2O_3 catalysts to the nickel content in the hydrogenation of benzene was studied by Selwood [11], who showed that with reduction of the concentration of nickel in the catalyst, which was prepared by a method analogous to that described here, to below 8%, its activity falls very sharply. We measured the activities of catalysts containing 5, 10, and 15% of nickel in the hydrogenolysis of toluene to benzene, and the first sample was practically inactive. Supplementary impregnation of the inactive catalyst (up to 5% of nickel) by the same method as was used in the preparation of the catalyst led to the recovery of the original activity. These examples give a graphic confirmation of the view that the deactivation of the catalyst is indeed due to the reduction of the concentration of free nickel in the catalyst.

Since γ-Al_2O_3 is used extremely widely in the preparation of catalysts, including industrial catalysts, as active component or as carrier, in work both with nickel-alumina and with catalysts of similar composition and structure the possibility of spinel formation must be constantly kept in mind.

The adsorption measurements were carried out by V. A. Afanas'ev, and the authors thank him for permission to make use of his results.

SUMMARY

In the oxidative stage of the regeneration of an Ni − Al_2O_3 catalyst at about 500° there is partial spinel formation, which leads to reduction in the content of free nickel after the reduction of the catalyst and to reduction in the activity of the latter.

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ALKYLATION OF ANISOLE AND PHENETOLE
WITH ISOAMYLENES

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There is little information in the literature on the alkylation of alkyl phenyl ethers, though the alkylation of phenol ethers presents considerable interest [1, 2]. The alkylation of anisole with trimethylethylene in presence of titanium tetrachloride was described by Cullinan [3], who obtained p-t-pentylanisole in 67% yield. The alkylation of phenetole with propene in presence of phosphoric acid was carried out by Ipatieff and co-workers [4]. Also, as catalysts in this reaction the molecular compounds of boron trifluoride [5-7] and some molybdates [8] have been studied.

In continuation of our work on the alkylation of phenols with amylenes [9, 10] we carried out the alkylation of anisole and phenetole with isoamylenes in presence of zinc chloride on alumina in an autoclave at 150-200°, and also in presence of Kationit KU-1 at 90-100° at atmospheric pressure. As a result of experiments on the alkylation of anisole with isoamylenes in presence of zinc chloride on alumina at 150° we isolated p-t-pentylanisole in 49% yield and 2,4-di-t-pentylanisole in 6% yield. Rise in the alkylation temperature to 200° led to an insignificant rise in the yields (51% and 8%, respectively). In the alkylation of phenetole under the same conditions (200°) we obtained p-t-pentylphenetole in 47% yield and 2,4-di-t-pentylpenetole in 6% yield. In the alkylation of anisole and phenetole with trimethylethylene in presence of the acidic Kationite KU-1 at 95-100° and atmospheric pressure the yields of p-t-pentylanisole and p-t-pentylphenetole were 13.5% and 20% respectively. An attempt to alkylate anisole and phenetole in presence of KU-1 in an autoclave was not successful.

EXPERIMENTAL

An autoclave was charged with 0.32 mole of anisole (or phenetole), 0.4 mole of isoamylenes [b.p. 19-38° (745 mm)], and 3.6 g of catalyst, i.e., zinc chloride (20%) deposited on alumina (80%). The catalyzates were washed with alkali and with water, dried, and vacuum-fractionated through a column of 20 plate efficiency. Under these conditions the amount of cleavage of the ether link was insignificant: the amount of acidic products isolated was 1-2%. The experiments with Kationit KU-1 were carried out in a three-necked flask fitted with condenser, stirrer, and dropping funnel. The flask was charged with 0.3 mole of anisole (or phenetole), 0.4 mole of trimethylethylene, and 12.8 g of Kationit. The reaction was carried out with heating in a boiling water bath for 6-8 hours. From the catalyzates obtained in the alkylation of anisole with a mixture of isoamylenes in presence of zinc chloride on alumina at 200° we isolated: 1) p-t-Pentylanisole (51% yield); b.p. 82-84° (5 mm); n_D^{20} 1.5045; d_4^{20} 0.9467. The literature [11] gives: b.p. 225-228° (735 mm); n_D^{20} 1.4990; d_4^{20} 0.9430. 2) 2,4-Di-t-pentylanisole (8% yield); b.p. 106-109° (5 mm); n_D^{20} 1.4960; d_4^{20} 0.9298. Found: C 82.6, 82.4; H 11.53, 11.37%; MR 78.36. $C_{17}H_{28}OF_3$. Calculated: C 82.20; H 11.36%; MR 78.74.

From the experiments on the alkylation of phenetole we isolated: 3) p-t-Pentylphenetole (yield 47%); b.p. 95-97° (5 mm); n_D^{20} 1.5025; d_4^{20} 0.9315; MR 60.85. $C_{13}H_{20}OF_3$. Calculated: MR 60.28. 4) 2,4-Di-t-pentyl-phenetole (yield 5%); b.p. 123-126° (5 mm); n_D^{20} 1.4950; d_4^{20} 0.9177. Found: C 82.46, 82.29; H 11.53, 11.47%. MR 83.26. $C_{18}H_{30}O_3F_3$. Calculated: C 82.40; H 11.44%; MR 83.36.

To confirm the structures of the alkylated ethers obtained these were converted into the corresponding phenols by the procedure described by Alls [12]: heating of 22 g of the alkylated ether with 100 g of glacial acetic acid saturated with hydrogen bromide in a bomb for 3.5 hours at 95-100°. By the cleavage of p-t-pentylanisole and p-t-pentylphenetole we obtained p-t-pentylphenol; b.p. 142-142.5° (20 mm); m.p. (from petroleum ether) 92-93°.

The literature [13] gives m.p. 92-93°. In the cleavage of the disubstituted anisole and phenetole only p-t-pentyl-anisole (m.p. 92-93°) was obtained.* It is probable that under the given conditions the t-pentyl group in the ortho position was split off.

SUMMARY

1. By the alkylation of anisole and phenetole with isoamylenes in presence of zinc chloride on alumina at 200°, p-t-pentylanisole, p-t-pentylphenetole, and also the 2,4-disubstituted compounds, were obtained.

2. Alkylation of anisole and phenetole in presence of Kationit KU-1 at 100° and atmospheric pressure gives low yields of p-t-pentylanisole and p-t-pentylphenetole.

3. The cleavage of 2,4-di-t-pentylanisole and 2,4-di-t-pentylphenetole by heating them with acetic acid saturated with hydrogen bromide leads to the elimination of the t-pentyl group in the ortho position.

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* This appears to be an error; p-t-pentylphenol is probably meant. — Publisher.

DISPERSITY AND ELECTRICAL PROPERTIES OF AEROSOLS
ARISING IN THE RADIOLYSIS OF GASEOUS HYDROCARBONS

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As shown previously [1, 2], in the radiolysis of gaseous hydrocarbons, and also of their mixtures with oxygen, liquid and solid products resulting from radiation-induced chemical reactions are found in the aerosol state, and the amount of the disperse phase depends on various conditions: dosage, intensity of the radiation, etc.

EXPERIMENTAL

We studied the dispersity and electrical properties of aerosols arising in the radiolysis of methane, ethane, propane, butane, ethylene, 4 : 1 methane-oxygen mixture, and 1 : 1 ethylene-oxygen mixture. The radiolysis was carried out in a two-liter metal reactor with the aid of an accelerator giving accelerated electrons of mean energy, after passage through the exit window, of 112 kev.

The aerosols formed were investigated by the photographic oscillation method [3, 4], which consists in the photography of the zig-zag trajectories of the particles falling under the force of gravity in a horizontal electrical field which varies periodically in direction, but is constant in value. The p.d. across the plates of the condenser was set at 80 v, their distance apart was 2.08 mm, and the commutation of the direction of the electrical field had a period of 2 seconds. As the dispersion medium was a gas subjected to irradiation, in the calculation of the dimensions and charges of the particles the appropriate viscosity coefficients were used. The density of the liquid drops was taken to be equal to that of the condensate, which was determined with a pycnometer and for the aerosols obtained by the radiolysis of CH_4, C_2H_6, C_3H_8, $n-C_4H_{10}$, C_2H_4, and $C_2H_4 + O_2$ was respectively 0.8015, 0.8129, 0.8095, 0.7816, 0.8603, and 1.0823; the density of the condensate obtained by the irradiation of the mixture $CH_4 + O_2$ was calculated from chemical analytical data and found to be 1.1120 g/cc. Cunningham's correction was not taken into account in the calculations. In all cases the aerosols were prepared in a concentration of 1 mg/liter, which was determined with a special SPP filter. Lower concentrations were inexpedient, for they are not characteristic for radiation-induced gas reactions proceeding under the conditions of our experiments, and aerosols of higher weight concentrations are too unstable, so that it is difficult to investigate them, even with such a rapid method as the photographic oscillation method.

Fig. 1. Size distribution of particles in aerosols formed in the radiolysis of: 1) Methane; 2) ethane; 3) propane; 4) butane.

Count concentrations were determined by a VDK-4 flow ultramicroscope working in accordance with the method published in [5]. The results of dispersity measurements are presented as differential curves of the size distribution of the particles (obtained from the corresponding histograms) in Figs. 1 and 2, in which the ordinate represents the fraction of the particles in a radius range of 0.1μ. All experiments were carried out at room temperature with an electron beam of intensity $I = 100 \mu$ amp and a gas pressure in the reactor of $p = 1$ atm. The irradiation time was varied, depending on the gas irradiated, from 6 seconds to 30 minutes to obtain a concentration of 1 mg/liter.
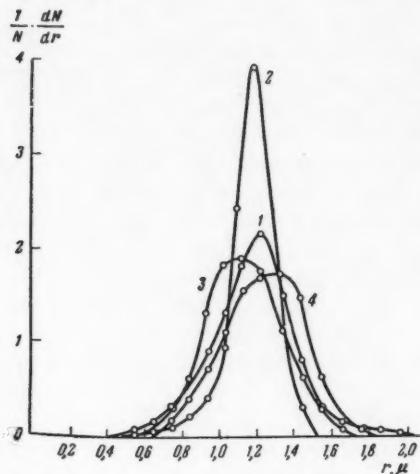
Irradiated gas or mixture of gases	Total number of particles measured	Proportion of charged particles (%)	Proportion of these particles charged		Charge on individual particle (in elementary charges)
			positively	negatively	
Methane	347	72,6	46,4	53,6	2—34
Ethane	346	67,2	50,0	50,0	1—38
Propane	270	78,5	47,6	52,4	2—13
Butane	312	74,2	49,0	51,0	2—22
Ethylene	464	62,5	51,8	48,2	1—35
Methane with oxygen	300	73,3	50,0	50,0	2—39
Ethylene with oxygen	359	65,2	52,5	47,5	5—67

The count concentrations of the aerosols formed in the irradiation of CH_4, C_2H_6, C_3H_8, C_4H_{10}, C_2H_4, $CH_4 + O_2$, and $C_2H_4 + O_2$ were equal respectively to: $5.8 \cdot 10^6$, $5.7 \cdot 10^6$, $6.0 \cdot 10^6$, $5.8 \cdot 10^6$, $6.0 \cdot 10^6$, $5.4 \cdot 10^6$, and $5.7 \cdot 10^6$ particles/cc.

Figure 1 gives the results of measurements for saturated hydrocarbons, namely methane, ethane, propane, and butane, and Fig. 2 gives the results for ethylene and the oxygen mixtures indicated above. The numbers of measured particles in the aerosols obtained by radiolysis were as follows: CH_4—252, C_2H_6—232, C_3H_8—212, n-C_4H_{10}—231, C_2H_4—290, $CH_4 + O_2$—220, and $C_2H_4 + O_2$—234. As will be seen from Figs. 1 and 2, the dimensions of the particles were found to be distributed in the range of radii from 0.4 to 2 μ, and the bulk of the particles was distributed in a still narrower range, from 0.9 go 1.5 μ. In the experiment with ethylene the curve was displaced somewhat toward the lower radii, and in the experiment with the mixture $C_2H_4 + O_2$ it was displaced toward the larger radii.
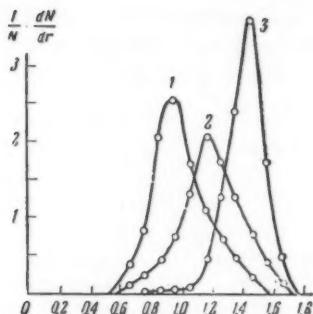
Fig. 2. Size distribution of particles in aerosols formed in the radiolysis of: 1) ethylene; 2) mixture of methane and oxygen; 3) mixture of ethylene and oxygen.

As the method used enabled us to make measurements over a period of several minutes, during which time the aerosol systems did not change appreciably, the data obtained in the experiment with CH_4 must be regarded as more correct than those which we obtained by the method of the vertical electric field [1], in which, as was to be expected, the bulk of the particles were distributed in the region of somewhat smaller radii. All the curves have fairly sharp maxima. Thus, for the aerosol formed in the radiolysis of ethane about 90% of the particles fall in the radius range 1.0 - 1.4 μ; for the aerosol formed in the radiation-induced oxidation of ethylene 88% of the particles have radii in the range 1.2-1.6 μ; and in the aerosol formed in the irradiation of butane 75% of the particles have radii in the range 1.0-1.5 μ. Hence, the aerosol systems formed have a fair degree of polydispersity. The disperities of aerosols formed in radiation-induced reactions may obviously vary, depending on the intensity of the radiation and of the energy absorbed. Thus, it was noted that if the integral dose is reduced tenfold in the irradiation of methane aerosols of higher dispersity are formed. The formation of aerosols in the radiolysis of gaseous hydrocarbons occurs, on the one hand, by the mechanism of chemical condensation and moreover at room temperature; on the other hand, they are formed from the very beginning in a strongly ionized dipolar atmosphere. Thus, unlike condensation aerosols (physical or chemical condensation) obtained at low temperatures in absence of radiation [6], in which the proportion of charged particles is 10-20%, most of the particles of the present aerosols are charged. Since the expenditure of radiation energy in the formation of pairs of ions in the hydrocarbons investigated varies within narrow limits (from about 24 to 31 ev per pair of ions) the rate of formation of ions in our experiments can be taken to be about 10^{15} pairs of ions/cc·sec. The measurement of the charges on individual particles was carried out simultaneously with the determination of dispersity. The results are presented in the table.

As will be seen from the table, the aerosol particles are charged almost to an equal extent with positive and with negative charges, and the proportion of charged particles in the aerosols is 60-80%. Charges of various magnitudes were observed on the particles, but the bulk of the particles had charges lying within fairly narrow limits. Thus, for the aerosol obtained by the irradiation of propane 95% of the charged particles carried 2-8 elementary

charges; in the experiments with butane 85% of the particles carried 2-9 elementary charges, and in the experiments with ethylene and with ethylene mixed with oxygen 80% of the particles carried charges of 3-12 and 7-22 elementary charges, respectively. Hence, the particles were charged with a comparatively few charges of both signs.

SUMMARY

Aerosols formed in radiation-induced reactions consist of particles having radii of from 0.4 to $2\,\mu$. Up to 80% of all the particles are charged positively or negatively with charges amounting to 1-67 elementary charges.

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STRUCTURE OF THE TRIMER OF ACROLEIN
DIETHYL ACETAL

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In a study of the dimerization of acetals of α, β-unsaturated aldehydes under the influence of BF_3 etherate we showed that in the case of acrolein diethyl acetal the main reaction product was not the dimer, but a trimer of composition $C_{21}H_{42}O_6$. Its formation could not be explained by simple linear polymerization. It was found that the curve for the relation of the yield of trimer to the amount of catalysts has a characteristic maximum corresponding approximately to 1 mole of BF_3 per mole of trimer formed, while the yield of dimer (about 5%) under various reaction conditions (temperature, time, amount of catalyst) changed scarcely at all and was not related to the yield of trimer. This led us to suppose that the trimer is formed by an independent reaction in which the dimer is not an intermediate product.

The trimerization of aldehydes is well known and may be readily explained by the formation of quasi-aromatic complexes with subsequent stabilization with the aid of cyclic electron transfer. It is clear that for aldehyde acetals such a scheme is impossible. However, if we take account of the fact that in acrolein acetal the readily accessible double bond must be appreciably polarized, we may imagine the following reaction scheme for the trimerization of acrolein acetal:
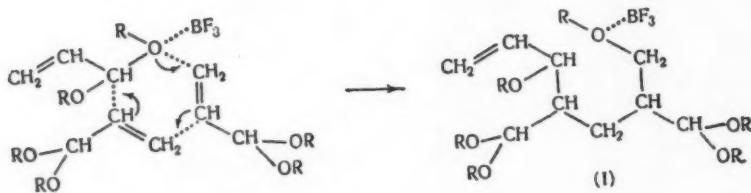
In the formation of the trimer of acrolein acetal a major part is played by the catalyst, whose addition to the acetal group brings about strong polarization of the $C-O$ bond. As a result there arises the possibility of the formation of a quasi-aromatic intermediate complex with six electrons in the field of six nuclei, the stabilization of which by the scheme of cyclic electron transfer [1, 2] leads to the trimer (I).

A study of the reactions of the trimer (I) confirms the proposed formula for this compound. Oxime formation shows that two carbonyl groups are present, and with 2,4-dinitrophenylhydrazine it gives a bisdinitrophenylhydrazone. Heating with 10% H_3PO_4 leads to the hydrolysis of two acetal groups with the formation of the dialdehyde (II) (b.p. 113-118° at 3 mm; n_D^{20} 1.4624), which is converted into the dicarboxylic acid (III) by oxidation with Ag_2O. According to catalytic hydrogenation data and the infrared spectrum of the trimer (I), this contains one isolated terminal double bond, and the acetal (IV) (b.p. 135-137° at 3 mm; n_D^{20} 1.4392) formed after hydrogenation and undergo analogous transformations with formation of the dialdehyde (V) (b.p. 101-105° at 2 mm; n_D^{20} 1.4620) and the diacid (VI). All these results support the view that the trimer (I) contains two acetal and two ethoxy groups. The position of one ethoxy group and the double bond with respect to the acetal group was proved with the aid of the spectra. In the hydrolysis of the trimer (I), as well as the ethoxy dialdehyde (II), there is an appreciable amount of the dialdehyde (VII) formed, and this contains two conjugated double bonds [λ_{max} 267 mμ (alcohol)]. Analogous hydrolysis of the saturated substance (IV) gave not only the diethoxy aldehyde (V), but also the α, β-unsaturated aldehyde (VIII) (1722, 1677, 1645 cm^{-1}). These data are in good accord with the formula proposed for the trimer (I).

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The 1,5-arrangement of the acetal groups was confirmed by the hydrogenolysis of the trimer over a mixture of Pt/C and PdCl$_2$ in glacial acetic acid. After the absorption of three molecular proportions of hydrogen the carbony-free product (IX) [b. p. 117-120° (4 mm); n_D^{20} 1.45341] was isolated. The infrared spectrum of this had only one broad band in the region of 1090 cm^{-1}, which corresponds to the vibrations of the C–O bond in ethers. Also, after hydrolysis of the trimer we succeeded in isolating a product of composition $C_{17}H_{32}O_5$, which according to the spectrum contained no carbonyl groups, but reacted with 2,4-dinitrophenylhydrazine. Analysis showed that this substance could not be unhydrolyzed acetal, and it probably had the cyclic structure (X). The formation of the anhydride (XI) (ν 1715, 1796 cm^{-1}) as impurity in the distillation of the acid (VI) in a high vacuum provides further confirmation of the position of the aldehyde groups in the trimer (I).
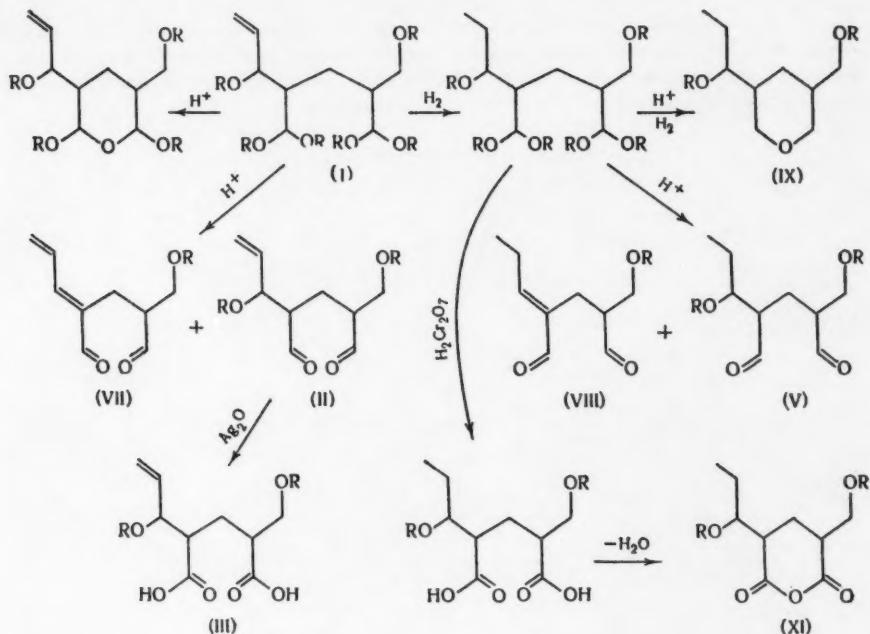
All the data examined lead us to suppose that the trimer of acrolein acetal has the structure of the diethyl acetal (I).

EXPERIMENTAL

To prepare the trimer of acrolein acetal 2 ml of BF$_3$ etherate was added to a mixture of 12.8 g of acrolein acetal [3] and 30 ml of dry ether at −30°, after which the mixture was stirred for one hour. The catalyst was neutralized with solid sodium bicarbonate. Distillation gave 1.1 g of dimer, 7.6 g (60%) of trimer fraction, b.p. 130-153° (1 mm) and n_D^{20} 1.4436, and 2.0 g of residue. After repeated fractionations we isolated the trimer (I); b.p. 170-173° (8 mm); n_D^{20} 1.4432; yield 40-50%. Found: C 64.35, 64.11; H 10.65, 10.71%; mol. wt. [4], average 383. $C_{21}H_{42}O_6$. Calculated: C 64.58; H 10.84%; mol. wt. 390.6.

Oxime formation: mean equiv. wt. found, 192.5; mol. wt. 385. 2,4-Dinitrophenylhydrazone, yellow precipitate, m.p. 207-208° (alcohol and petroleum ether); λ_{max} 366 mμ (alcohol). Found: C 49.64, 49.83; H 4.66, 4.67; N 19.04, 19.05%. $C_{25}H_{30}O_{10}N_8$. Calculated: C 49.85; H 4.98; N 18.6%.

We thank A. A. Slinkin and M. E. Vol'pin for participating in the work and discussing the results.

SUMMARY

The product formed by the condensation of acrolein diethyl acetal under the influence of BF$_3$ etherate is a trimer of composition $C_{21}H_{42}O_6$ and is 2-ethoxy-4-(1-ethoxyallyl)glutaraldehyde diethyl acetal. A mechanism is proposed for its formation via a quasi-aromatic complex with subsequent cyclic electron transfer.

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All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. *Some or all of this periodical literature may well be available in English translation.* A complete list of the cover-to-cover English translations appears at the back of this issue.

1-[2-(VINYLTHIO)ETHYL]-2-PYRROLIDINONE

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With the object of extending methods of synthesis and investigations based on lactams it was considered desirable to synthesize unsaturated compounds containing not only a lactam ring, but also sulfur. The polymerization of such substances could lead to products having new technical qualities. In the present work we studied the vinylation of 1-(2-mercaptoethyl)-2-pyrrolidinone, which was synthesized earlier [1].

$$\underset{NCH_2CH_2SH}{\overset{(CH_2)_3-CO}{\diagdown\diagup}} + CH\equiv CH \longrightarrow \underset{NCH_2CH_2SCH=CH_2}{\overset{(CH_2)_3-CO}{\diagdown\diagup}}$$
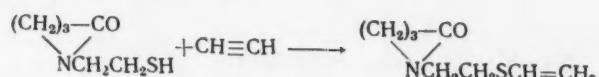
The vinylation of thiols containing lactam rings has not been described in the literature. There is a reference in a patent [2] to the synthesis of amino vinyl sulfides of general formula $CH_2 = CHSAN(R)R'$, in which A is a alkylene or phenylene and R and R' are H or a lower alkyl. The vinylation of amino thiols was carried out in butyl alcohol in presence of 12% potassium butoxide as catalyst. Polymers of amino vinyl sulfides have bactericidal properties, and they are added also in the spinning of cellulose acetate fibers to increase dyeability with acid dyes. We carried out the vinylation of 1-(2-mercaptoethyl)-2-pyrrolidinone in an autoclave in a dioxane medium with acetylene undiluted with inert gas and taken in two- to four-fold excess. Here there is no need to prepare a potassium alkoxide: vinylation proceeds smoothly and in good yield in presence of 10% of potassium hydroxide.

A study was made of some of the reactions of the 1-[2-(vinylthio)ethyl]-2-pyrrolidinone (I) synthesized: addition of thiols, polymerization, and copolymerization. The addition of thiols was brought about readily under the conditions of free-radical initiation (azobisisobutyronitrile); this gave the corresponding sulfides in yields of more than 80%:

$$\underset{NCH_2CH_2SCH=CH_2}{\overset{(CH_2)_3-CO}{\diagdown\diagup}} + RSH \xrightarrow[80-85°]{\substack{0.5\% \text{ of} \\ \text{azo dinitrile}}} \underset{NCH_2CH_2SCH_2CH_2SR}{\overset{(CH_2)_3-CO}{\diagdown\diagup}}$$
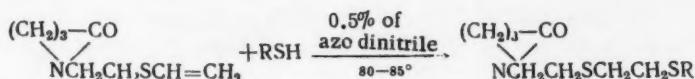
When heated, the monomer (I) undergoes thermal polymerization. The polymerization is accelerated by the addition of azobisisobutyronitrile. The new polymer is a clear, almost colorless, semisolid substance which shows a wide range of solubility: it is readily soluble in water, alcohol, benzene, and in other common organic solvents except diethyl ether and petroleum ether. In this respect the polymer of 1-[2-(vinylthio)ethyl]-2-pyrrolidinone is analogous to the polymers of 1-vinyl-2-pyrrolidinone and of 1-[2-(vinyloxy)ethyl]-2-pyrrolidinone [3]. It is evident that the character of the solubility of these polymers is determined mainly by the presence of the lactam ring. The monomer (I) forms not only homopolymers, but is able to undergo copolymerization with other vinyl monomers (see table). It was found that (I) is extremely reactive in copolymerization reactions: it is similar in activity to acrylonitrile and methyl acrylate and is considerably more reactive than vinyl acetate and 1-vinyl-2-pyrrolidinone. Earlier, in a study of the copolymerization of 2-butoxyethyl vinyl sulfide with vinylcaprolactam [4, 5] it was noted that in copolymerization the vinyl sulfide is more active than the vinyl lactam. Like the polymers obtained from the original monomers, the copolymer obtained from 1-vinyl-2-pyrrolidinone and (I) is soluble in water.

EXPERIMENTAL

Vinylation of 1-(2-mercaptoethyl)-2-pyrrolidinone. This was carried out in a 250 ml rotating autoclave fitted with a manometer and a thermocouple with automatic regulation of temperature. A mixture of 10 g of the thiol,

Properties of Polymers Obtained

Name	Appearance	Yield (%)	S found (%)	Content of (I) units in copolymer (moles %)	Solubility**						
					H_2O	C_2H_5OH	C_6H_6	acetone	N,N-di-methylfor-mamide	diethyl ether	petroleum ether
Homopolymer of the vinyl sulfide (I)	Clear elastic mass	44.3	18.75* 18.80	100	S	S	S	N	–	N	N
Copolymer of methyl acrylate and (I)	" "	47.3	13.01 13.16	43.3	N	S	S	S lim	–	N	N
Copolymer of (I) and vinyl acetate	Clear semisolid product	28.8	17.20 16.70	83.2	N	S	S	N	–	N	N
Copolymer of (I) and vinylpyrrolidinone	Clear elastic mass	54.0	14.90 14.92	72.3	S	S	S	S lim	–	N	N
Copolymer of (I) and acrylonitrile	White brittle solid	46.8	13.41 13.36	44.4	N	N	N	N	S	N	N

* Calculated for $C_8H_{13}ONS$ 18.72%.

** S = soluble; N = insoluble; S lim. = solubility limited.

1 g of KOH powder, and 30 ml of dioxane was placed in the autoclave, which was purged with nitrogen; acetylene was passed in twice, the whole was heated for two hours at 120°, and the apparatus was then left overnight. The reaction mixture was diluted with ether; after filtration and removal of solvents by distillation we obtained 9.6 g (81.8%) of substance of b.p. 137-138° (2.5 mm). Further purification of the product can be carried out by treating its dilute ether solution with sodium; after fractionation the product is analytically pure: b.p. 142-143° (3 mm); 132.5-133.5° (2 mm); n_D^{20} 1.5380; d_4^{20} 1.1222. Found: C 56.21; H 7.77; N 18.56%; MR 48.16. $C_8H_{13}ONS$. Calculated: C 56.11; H 7.65; N 18.72%; MR 48.39.

1-[2-(Vinylthio)ethyl]-2-pyrrolidinone (I) is a colorless viscous liquid, soluble in almost all organic solvents; it has not a pungent odor.

Addition of ethanethiol. A mixture of 5 g of (I), 4 g of the thiol, and 0.0247 g of azobisisobutyronitrile was heated in a sealed tube for six hours at 80-85°. Removal of excess of the thiol by distillation gave 5.9 g (88%) of reaction product as a viscous liquid, b.p. 117-120° (0.015 mm); after refractionation it had the following constants: b.p. 117-120° (0.015 mm); n_D^{20} 1.5440; d_4^{20} 1.1222; found MR 65.66; calculated MR 66.07; and it corresponded in analysis to 1-[2-[[2-(ethylthio)ethyl]thio]ethyl]-2-pyrrolidinone. Found: C 51.69; H 8.35; S 27.27; N 6.06%. $C_{10}H_{19}ONS_2$. Calculated: C 51.46; H 8.21; S 27.48; N 6.00%.

Addition of 1-butanethiol. Under the conditions of the preceding experiment from 4.2 g of (I), 3.4 g of 1-butanethiol, and 0.025 g of the azo dinitrile we obtained 6.2 g (82.6%) of 1-[2-[[2-(butylthio)ethyl]thio]ethyl]-2-pyrrolidinone.

After refractionation the sulfide had the following constants: b.p. 133-136° (0.03 mm); n_D^{20} 1.5340; d_4^{20} 1.0852. Found: C 55.23; H 8.91; S 24.37; N 5.13%; MR 74.88. $C_{12}H_{23}ONS_2$. Calculated: C 55.13; H 8.86; S 24.53; N 5.36%.

Polymerization and copolymerization. This was carried out under standard conditions in ampoules at 60° for 100 hours in presence of 0.2% of azobisisobutyronitrile. After the time indicated the ampoules were cooled. The solubilities of the polymeric products were determined qualitatively, and the polymers were then purified by the reprecipitation method and dried to constant weight. Copolymerization was carried out with mixtures of monomers in the proportions of 1 : 1. For the precipitation of the polymers and copolymers diethyl ether was used except in the case of the copolymer of (I) with methyl acrylate, for which the precipitant was petroleum ether. The results obtained are given in the table.

SUMMARY

1. 1-[2-(Vinylthio)ethyl]-2-pyrrolidinone was synthesized.

2. New water-soluble polymers were prepared by the polymerization of 1-[2-(vinylthio)ethyl]-2-pyrrolidinone and by its copolymerization with 1-vinyl-2-pyrrolidinone.

3. A study was made of the addition of alkanethiols to 1-[2-(vinylthio)ethyl]-2-pyrrolidinone under free-radical conditions.

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LETTERS TO THE EDITOR

ELECTRON PARAMAGNETIC RESONANCE SPECTRUM

OF β-CAROTENE

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There is a fairly large number of indications in the literature that compounds containing a considerable number of conjugated double bonds give a narrow electron paramagnetic resonance (EPR) signal characteristic for organic free radicals. It must be remembered that, because of the high sensitivity of the EPR method, an essential prerequisite for correct inferences is a careful investigation of the purity of the substance. There are many publications in which the authors come to far-reaching conclusions on the basis of EPR spectra, without having indicated the purity of the material under study and its identification.

In [1] there is the statement that "commercial" β-carotene gives an intense EPR signal. We decided to determine whether pure β-carotene does in fact give an EPR signal (β-carotene contains 11 conjugated double bonds). We had two samples of β-carotene: 1) synthetic β-carotene prepared in G. I. Samokhvalov's laboratory at the Vitamin Institute by the method described in [2]; m.p. 176°; 2) natural β-carotene purified in A. A. Krasnovskii's laboratory at the Institute of Biochemistry, Academy of Sciences, USSR, by repeated crystallization from carbon disulfide and benzene. For these samples of β-carotene we tried to find an EPR signal under various conditions:*
a) at room temperature in air; b) at room temperature in a vacuum and in an argon atmosphere; and c) at an elevated temperature (up to 130°) in argon and in air. Under none of these conditions was an EPR signal detected. It would appear that the presence of a considerable number of conjugated double bonds in a molecule is still not sufficient to confer free-radical properties on a molecule or to enable it to exist in the triplet state in ordinary conditions.

The authors thank A. A. Krasnovskii, G. I. Samokhvalov, N. N. Drozdova, and L. A. Vakulova for the presentation of preparations.

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* The investigations were carried out on a radiospectrometer [3] with high-frequency magnetic field modulation and automatic adjustment of the klystron generator frequency with respect to the working resonator with a sensitivity of about 10^{-11} mole in the sample with respect to diphenylpicrylhydrazyl.

VAPOR-PHASE CATALYTIC KETONIZATION OF ACETIC
ACID OVER QUADRIVALENT-METAL OXIDES AND BeO

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In a comparison of the kinetics of the catalytic ketonization of CH_3COOH over the oxides and carbonates of Group II metals and the results of a structural investigation of these catalysts [1] with the kinetics of the reaction over quadrivalent-metal oxides and their structures before and after the experiments, we established appreciable differences in reaction mechanism. Over MgO, ZnO, CdO, $MgCO_3$, $CaCO_3$, $SrCO_3$, and $BaCO_3$ the reaction proceeds with the intermediate formation of acetate throughout the whole volume of the catalyst. In the case of TiO_2, ZrO_2, SnO_2, CeO_2, and also BeO, the acetate phase was not detected in the volume of the catalysts, so that the reaction proceeds only at the surface. The same is indicated by the relation of the specific surfaces of these catalysts to their activities. We consider that the cause of the observed differences lies in the greater strengths of the crystal lattices of MO_2 and BeO, due to the oxane state of the oxygen [2]. The results obtained lead to suppose that on MO_2 and BeO CH_3COOH is bound to the surface with hydrogen bonds in which there participate either the oxygen of the carbonyl group and the hydrogen of an OH group present on the oxide surface, or the hydrogen of the hydroxyl of the acid and the oxygen of the metal oxide. It is probable that the formation of the reaction products proceeds via an active cyclic complex formed by two CH_3COOH molecules on the hydrated or nonhydrated surface of MO_2 and BeO.

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INVESTIGATION OF CHARGE EXCHANGE OF THE THERMAL IONS A^+, Kr^+, AND Xe^+ BY THE IMPULSE METHOD FOR THE MOLECULES CH_4, C_2H_6, AND C_2H_4

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In the investigation of elementary processes of charge exchange of ions for the case of molecules in the ion source of a mass spectrometer at pressures of 10^{-4} mm, the main difficulty is the distinguishing of secondary ions on an extensive background of primary ions that coincide strictly with the secondary ions in mass and charge. As a way of distinguishing these the authors proposed the method of impulse ionization, which was developed by one of us with Frankevich [1] for measuring rate constants for the reactions of thermal ions with molecules. The ions are formed in the source by a microsecond impulse of electrons; the drawing of the ions from the ionization region occurs only after 15-20 μsec, during which the scatter of the ions is determined mainly by thermal velocities. As a result of the increase in the time spent by the primary ions in the ionization region, the yield of the reactions rises substantially. The method becomes particularly effective when the mass of the striking ion is substantially greater than the mass of the primary "background" ion. The authors have succeeded in obtaining coefficients of enrichment of the ion beam by secondary ions of 10^2, as compared with the results of the usual, nonimpulse, method.

It was found that in the collisions of these ions and molecules there occur mainly processes of dissociative charge exchange with cross sections of 10^{-14} cm^2, and the spectrum of the ion fragments formed is very close to that formed in the charge exchange of the same ions of energy 300-500 ev. Results were obtained which indicate that an appreciable part of the Kr^+ and Xe^+ ions are formed and react with molecules in the excited state $^2P_{1/2}$.

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SIGNIFICANCE OF ABBREVIATIONS MOST FREQUENTLY
ENCOUNTERED IN SOVIET PERIODICALS

FIAN	Phys. Inst. Acad. Sci. USSR
GDI	Water Power Inst.
GITI	State Sci.-Tech. Press
GITTL	State Tech. and Theor. Lit. Press
GONTI	State United Sci.-Tech. Press
Gosenergoizdat	State Power Press
Goskhimizdat	State Chem. Press
GOST	All-Union State Standard
GTTI	State Tech. and Theor. Lit. Press
IL	Foreign Lit. Press
ISN (Izd. Sov. Nauk)	Soviet Science Press
Izd. AN SSSR	Acad. Sci. USSR Press
Izd. MGU	Moscow State Univ. Press
LEIIZhT	Leningrad Power Inst. of Railroad Engineering
LET	Leningrad Elec. Engr. School
LETI	Leningrad Electrotechnical Inst.
LETIIZhT	Leningrad Electrical Engineering Research Inst. of Railroad Engr.
Mashgiz	State Sci.-Tech. Press for Machine Construction Lit.
MEP	Ministry of Electrical Industry
MES	Ministry of Electrical Power Plants
MESEP	Ministry of Electrical Power Plants and the Electrical Industry
MGU	Moscow State Univ.
MKhTI	Moscow Inst. Chem. Tech.
MOPI	Moscow Regional Pedagogical Inst.
MSP	Ministry of Industrial Construction
NII ZVUKSZAPIOI	Scientific Research Inst. of Sound Recording
NIKFI	Sci. Inst. of Modern Motion Picture Photography
ONTI	United Sci.- Tech. Press
OTI	Division of Technical Information
OTN	Div. Tech. Sci.
Stroiizdat	Construction Press
TOE	Association of Power Engineers
TsKTI	Central Research Inst. for Boilers and Turbines
TsNIEL	Central Scientific Research Elec. Engr. Lab.
TsNIEL-MES	Central Scientific Research Elec. Engr. Lab.-Ministry of Electric Power Plants
TsVTI	Central Office of Economic Information
UF	Ural Branch
VIESKh	All-Union Inst. of Rural Elec. Power Stations
VNIIM	All-Union Scientific Research Inst. of Metrology
VNIIZhDT	All-Union Scientific Research Inst. of Railroad Engineering
VTI	All-Union Thermotech. Inst.
VZEI	All-Union Power Correspondence Inst.

NOTE: Abbreviations not on this list and not explained in the translation have been transliterated, no further information about their significance being available to us. —Publisher.

Soviet Journals Available in Cover-to-Cover Translation

ABBREVIATION	RUSSIAN TITLE	TITLE OF TRANSLATION	PUBLISHER	Vol.	Issue	Year
AÉ	Atomnaya énergiya	Soviet Journal of Atomic Energy	Consultants Bureau	1	1	1956
Akust. zh.	Akusticheskii zhurnal	Soviet Physics – Acoustics	American Institute of Physics	1	1	1955
	Antibiotiki	Antibiotics	Consultants Bureau	4	1	1959
Astr(on). zh(urn).	Astronomicheskii zhurnal	Soviet Astronomy—AJ	American Institute of Physics	34	1	1957
Avto(mat). svarka	Avtomaticheskaya svarka	Automatic Welding	British Welding Research Association (London)			
	Avtomatika i Telemekhanika	Automation and Remote Control	Instrument Society of America	27	1	1959
	Biofizika	Biophysics	National Institutes of Health*		1	1956
	Biokhimiya	Biochemistry	Consultants Bureau	21	1	1957
Byull. éksp(erim). biol. i med.	Byulleten' éksperimental'noi biologii i meditsiny	Bulletin of Experimental Biology and Medicine	Consultants Bureau	41	1	1959
DAN (SSSR) / Dok(lady) AN SSSR	Doklady Akademii Nauk SSSR	The translation of this journal is published in sections, as follows:				
		Life Sciences — Doklady Biochemistry Section	American Institute of Biological Sciences	106	1	1956
		Doklady Biological Sciences Sections (includes: Anatomy, biophysics, cytology, ecology, embryology, endocrinology, evolutionary morphology, genetics, histology, hydrobiology, microbiology, morphology, parasitology, physiology, zoology sections)	American Institute of Biological Sciences	112	1	1957
		Doklady Botanical Sciences Sections (includes: Botany, phytopathology, plant anatomy, plant ecology, plant embryology, plant physiology, plant morphology sections)	American Institute of Biological Sciences	112	1	1957
		Chemical Sciences — Proceedings of the Academy of Sciences of the USSR, Section: Chemical Technology	Consultants Bureau	106	1	1956
		Proceedings of the Academy of Sciences of the USSR, Section: Chemistry	Consultants Bureau	106	1	1956
		Proceedings of the Academy of Sciences of the USSR, Section: Physical Chemistry	Consultants Bureau	112	1	1957
		Earth Sciences — Doklady Earth Sciences Sections (includes: Geochemistry, geology, geophysics, hydrogeology, mineralogy, paleontology, petrography, permafrost sections)	American Geological Institute	124	1	1959
		Proceedings of the Academy of Sciences of the USSR, Section: Geochemistry	Consultants Bureau	106-123	6	1957-1958
		Proceedings of the Academy of Sciences of the USSR, Sections: Geology	Consultants Bureau	106-123	6	1958
		Mathematics — Doklady Soviet Mathematics	The American Mathematics Society	131	1	1961
		Physics — Soviet Physics—Doklady (includes: Aerodynamics, astronomy, crystallography, cybernetics and control theory, electrical engineering, energetics, fluid mechanics, heat engineering, hydraulics, mathematical physics, mechanics, physics, technical physics, theory of elasticity sections)	American Institute of Physics	106	1	1956
		Proceedings of the Academy of Sciences of the USSR, Applied Physics Sections (does not include mathematical physics or physics sections)	Consultants Bureau	106-117	1	1956-1957
Derevoobrabat. prom-st'.	Derevoobrabatyvayushchaya promyshlennost'	Wood Processing Industry	Timber Development Association (London)			
Élecktrosvyaz	Élecktrosvyaz	Telecommunications	Massachusetts Institute of Technology*		9	1959
Entom(ol). oboz(renie)	Entomologicheskoe obozrenie	Entomological Review	American Institute of Biological Sciences	38	1	1957
Farmakol. (i) toksikol(ogiya)	Farmakologiya i toksikologiya	Pharmacology and Toxicology	Consultants Bureau	20	1	1959
FMM	Fizika metallov i metallovedenie	Physics of Metals and Metallography	Acta Metallurgica*	5	1	1957
Fiziol. zhurn. SSSR (im. Sechenova)	Fiziologicheskii zhurnal im. I. M. Sechenova	Sechenov Physiological Journal USSR	National Institutes of Health*		1	1957
Fiziol(ogiya) rast.	Fiziologiya rastenii	Plant Physiology	American Institute of Biological Sciences	4	1	1957
	Geokhimiya	Geochemistry	The Geochemical Society		1	1958
FTT	Fizika tverdogo tela	Soviet Physics—Solid State	American Institute of Physics	1	1	1959
Izmerit. tekh(nika)	Izmeritel'naya tekhnika	Measurement Techniques	Instrument Society of America		1	1959
Izv. AN SSSR, O(td). Kh(im). N(auk)	Izvestiya Akademii Nauk SSSR: Otdelenie khimicheskikh nauk	Bulletin of the Academy of Sciences of the USSR: Division of Chemical Sciences	Consultants Bureau		1	1952

continued

Abbreviation	Journal (transliterated)	English Title	Sponsoring Organization	No.	Year
Izv. AN SSSR, O(td). T(ekhn). N(auk). Met(all). i top.	(see Met. i top.)				
Izv. AN SSSR Ser. fiz(ich).	Izvestiya Akademii Nauk SSSR: Seriya fizicheskaya	Bulletin of the Academy of Sciences of the USSR: Physical Series	Columbia Technical Translations	1	1954
Izv. AN SSSR Ser. geofiz.	Izvestiya Akademii Nauk SSSR: Seriya geofizicheskaya	Bulletin (Izvestiya) of the Academy of Sciences USSR: Geophysics Series	American Geophysical Union	1	1954
Izv. AN SSSR Ser. geol.	Izvestiya Akademii Nauk SSSR: Seriya geologicheskaya	Izvestiya of the Academy of Sciences of the USSR: Geologic Series	American Geological Institute	1	1958
Kauch. i rez.	Kauchuk i rezina	Soviet Rubber Technology	Research Association of British Rubber Manufacturers	18	1959
				1	1960
	Kinetika i kataliz	Kinetics and Catalysis	Consultants Bureau	1	1958
	Koks i khimiya	Coke and Chemistry USSR	Coal Tar Research Association (Leeds, England)	1	1952
Kolloidn. zh(urn).	Kolloidnyi zhurnal	Colloid Journal	Consultants Bureau	14	1957
	Kristallografiya	Soviet Physics — Crystallography	American Institute of Physics	2	1958
Metalov. i term. obrabot. metal.	Metallovedenie i termicheskaya obrabotka metallov	Metal Science and Heat Treatment of Metals	Acta Metallurgica	1	1957
Met. i top.	Metallurg	Metallurgist	Acta Metallurgica	6	1960
	Metallurgiya i topliva	Russian Metallurgy and Fuels	Eagle Technical Publications	1	1957
Mikrobiol.	Mikrobiologiya	Microbiology	American Institute of Biological Sciences	1	1959
OS	Optika i spektroskopiya	Optics and Spectroscopy	American Institute of Physics	25	1958
	Pochvovedenie	Soviet Soil Science	American Institute of Biological Sciences	6	1959
	Priborostroenie	Instrument Construction	British Scientific Instrument Research Association	1	1957
Pribory i tekhn. éks(perimenta)	Pribory i tekhnika éksperimenta	Instruments and Experimental Techniques	Instrument Society of America	1	1958
Prikl. matem. i mekh.	Prikladnaya matematika i mekhanika	Applied Mathematics and Mechanics	American Society of Mechanical Engineers	1	1958
PTÉ	(see Pribory i tekhn. éks.)				
Radiotekh.	Problemy Severa	Problems of the North	National Research Council of Canada	12	1957
Radiotekh. i élektronika	Radiotekhnika	Radio Engineering	Massachusetts Institute of Technology*	2	1957
	Radiotekhnika i élektronika	Radio Engineering and Electronics	Massachusetts Institute of Technology*	1	1959
	Stanki i instrument	Machines and Tooling	Production Engineering Research Assoc.	1	1959
	Stal'	Stal (In English)	Iron and Steel Institute	1	1959
Stek. i keram.	Steklo i keramika	Glass and Ceramics	Consultants Bureau	13	1956
Svaroch. proiz-vo	Svarochnoe proizvodstvo	Welding Production	British Welding Research Association	4	1959
Teor. veroyat. i prim.	Teoriya veroyatnostei i ee primenenie	Theory of Probability and Its Applications	Society for Industrial and Applied Mathematics	1	1956
Tsvet. Metal'ly	Tsvetnye metally	Nonferrous Metals	Primary Sources	1	1960
UFN	Uspekhi fizicheskikh Nauk	Soviet Physics — Uspekhi (partial translation)	American Institute of Physics	66	1958
UKh	Uspekhi khimii	Russian Chemical Reviews	The Chemical Society (London)	1	1960
UMN	Uspekhi matematicheskikh nauk	Russian Mathematical Surveys	London Mathematical Society	15	1960
Usp. fiz. nauk	(see UFN)				
Usp. khim(ii)	(see UKh)				
Usp. matem. nauk	(see UMN)				
Usp. sovr. biol.	Uspekhi sovremennoi biologii	Russian Review of Biology	Oliver and Boyd	48	1959
Vest. mashinostroeniya	Vestnik mashinostroeniya	Russian Engineering Journal	Production Engineering Research Assoc.	4	1959
Vop. gem. i per. krovi	Voprosy gematologii i perelivaniya krovi	Problems of Hematology and Blood Transfusion	National Institutes of Health*	1	1957
Vop. onk.	Voprosy onkologii	Problems of Oncology	National Institutes of Health*	1	1957
Vop. virusol.	Voprosy virusologii	Problems of Virology	National Institutes of Health*	1	1957
Zavod(odsk) lab(oratoriya)	Zavodskaya laboratoriya	Industrial Laboratory	Instrument Society of America	25	1959
ZhAKh Zh. anal(it). khimii	Zhurnal analiticheskoi khimii	Journal of Analytical Chemistry USSR	Consultants Bureau	7	1952
ZhETF	Zhurnal éksperimental'noi i theoreticheskoi fiziki	Soviet Physics—JETP	American Institute of Physics	28	1955
Zh. éksperim. i teor. fiz.					
ZhFKh Zh. fiz. khimii	Zhurnal fizicheskoi khimii	Russian Journal of Physical Chemistry	The Chemical Society (London)	7	1959
ZhMÉi Zh(urn). mikrobiol. épidemiol. i immunobiol.	Zhurnal mikrobiologii, épidemiologii i immunobiologii	Journal of Microbiology, Epidemiology and Immunobiology	National Institutes of Health*	1	1957
ZhNKh	Zhurnal neorganicheskoi khimii	The Russian Journal of Inorganic Chemistry	The Chemical Society (London)	1	1959
Zh(urn). neorgan(ich). khim(ii)					
ZhOKh	Zhurnal obshchei khimii	Journal of General Chemistry USSR	Consultants Bureau	19	1949
Zh(urn). obshch(ei) khimii					
ZhPKh	Zhurnal prikladnoi khimii	Journal of Applied Chemistry USSR	Consultants Bureau	23	1950
Zh(urn). prikl. khimii					
ZhSKh	Zhurnal strukturnoi khimii	Journal of Structural Chemistry	Consultants Bureau	1	1960
Zh(urn). strukt. khimii					
ZhTF	Zhurnal teknicheskoi fiziki	Soviet Physics—Technical Physics	American Institute of Physics	26	1956
Zh(urn). tekhn. fiz.					
Zh(urn). vyssh. nervn. deyat. (im. Pavlova)	Zhurnal vysshei nervnoi deyatel'nosti (im. I. P. Pavlova)	Pavlov Journal of Higher Nervous Activity	National Institutes of Health*	1	1958